(54) **CARBIDE NANOMATERIALS**

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(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: **08/477,080**

(22) Filed: **Jun. 7, 1995**

(51) Int. Cl.^{7} **D01F 9/08**; D01F 9/12

(52) U.S. Cl. **423/439**; 423/440; 423/447.2; 423/414; 428/366; 428/367

(58) Field of Search .... 423/439, 440, 423/445 B, DIG. 39, DIG. 40, 447.2, 414; 428/366, 367

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(57) **ABSTRACT**

A nanoscale carbide article consisting essentially of covalently bounded elements M^1, M^2, and C having the molar ratio $M^1:M^2:C::1:y:x$, wherein the article has an aspect ratio of between 10 and 1000 and has a shorter axis of between 1 and 40 nanometers.

2 Claims, No Drawings

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CARBIDE NANOMATERIALS

STATEMENT AS TO FEDERALLY SPONSORED RESEARCH

BACKGROUND OF THE INVENTION

The invention is in the field of nanometer scale materials.

Examples of nanomaterials include hollow carbon graphite tubes with diameters between 1 and 75 nm, and lengths up to one micron. Such nanotubes are produced, for example, in reactors at 550–850° C. by mixing hydrogen and carbon-containing gases in the presence of a catalyst. Strategies used to prepare filled nanotubes include in-situ arc growth using metal/carbon composites and the loading of nanotubes using liquid reagents. In addition, graphitecoated, partially-hollow lanthanum carbide particles with overall diameters between 20 and 40 nm have been made.

In contrast to nanoscale materials, whiskers are crystalline solid structures generally having diameters between 1–100 microns, although diameters as small as 0.1 microns have been observed.

SUMMARY OF THE INVENTION

The invention features a carbide article consisting essentially of covalently bonded elements M^1, M^2 and C having the molar ratio M^1:M^2:C::1:y:x. The first element M^1 is selected from the first element group consisting of titanium, silicon, niobium, iron, boron, tungsten, molybdenum, zirconium, hafnium, vanadium, tantalum, chromium, manganese, technetium, rhenium, osmium, cobalt, nickel, a lanthanide series element, scandium, yttrium, and lanthanum. The second element M^2 is selected from a second element group consisting of nitrogen, boron, phosphorus, zinc, aluminum, copper, germanium, cadmium, indium, tin, lead, thallium, and the elements in the first element group, provided that the first and second elements are not the same. The value of y is between 0 and 0.9 (e.g., y is 0 or y is between 0.1 and 0.9). The third element C is sp^3 hybridized carbon, and the value of x is between 0.1 and 2.1 (e.g., between 0.9 and 1.1). The article has an aspect ratio of between 10 and 1000 (e.g., between 50 and 500, or between 100 and 1000), and has a shorter axis of between 1 and 40 nanometers (e.g., between 1 and 30 nm).

In certain embodiments, the article has a single crystal structure, a polycrystalline structure, or an amorphous structure. Preferably, element M^1 is selected from the group consisting of titanium, silicon, niobium, iron, boron, tungsten, molybdenum, or gadolinium, or from the group consisting of titanium and silicon. Preferably, second element M^2 is selected from the group consisting of boron and nitrogen, wherein y is greater than 0 (e.g., between 0.1 and 0.9). In one aspect, the article is a nanorod.

The nanoscale carbide articles of the invention are useful materials having metallic, semiconducting, insulating, superconducting, or magnetic properties, or a combination thereof. The novel dimensions of the disclosed articles permit the building of nanostructures and superior metallic, ceramic, and polymer composites. For example, the tensile strength (kg/mm^2) of the disclosed nanorods is greater than that of the corresponding whisker. Some embodiments have a lower density of stacking faults, as measured by TEM and

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normalized to diameter, than prior larger materials. For example, SiC nanorods disclosed herein have a lower density of stacking faults than the SiC whiskers as described by G. McMahon et al., *J. Mater. Sci.* 26:5655–5663 (1991). The invention encompasses not only the individually identified carbide articles, but also other nanoscale materials that are made according to processes disclosed herein. The invention also encompasses the methods disclosed herein for making carbide articles such as nanorods.

Other features or advantages of the present invention will be apparent from the following detailed description of the invention, and also from the appending claims.

Terms

As used herein, the term "carbide" means a compound of carbon and one or two elements more electropositive than carbon, excluding hydrogen. The atoms in a carbide are covalently bound, the carbon atoms being generally sp^3 hybridized as in Ta_2C and Cr_3C_2. In contrast, pure graphitic carbon (e.g., nanotube starting material) is sp^2 hybridized. Examples of binary carbides include TiC_x, NbC_x, and SiC_x (wherein x is between 0.5 and 1.1), Fe_3C_x (wherein x is between 0.8 and 1.2), and BC_x (wherein x is between 0.1 and 0.3). Additional examples of binary carbides include ZrC_x, HfC_x, VC_x, TaC_x, CrC_x, MoC_x, WC_x, NiC_x, LaC_x, CeC_x, PrC_x, NdC_x, SmC_x, GdC_x, DyC_x, HoC_x, ErC_x, and YbC_x. Examples of ternary carbides include carbonitrides, carboborides, and carbosilicides and others such as TiN_yC_x, MoN_yC_x, and SiN_yC_x, TiB_yC_x, $TiTa_yC_x$, $TiSi_yC_x$, $TiNb_yC_x$, $MoSi_yC_x$, MoB_yC_x, $MoGa_yC_x$, $MoAl_yC_x$, FeB_yC_x, $FeSi_yC_x$, $FeNi_yC_x$, SiB_yC_x, $TaSi_yC_x$, WSi_yC_x, $ZrSi_yC_x$, $NbSi_yC_x$, $CrSi_yC_x$, NdB_yC_x, and WCo_yC_x. The values of x and y are, respectively, between 0.1 and 2.1 and between 0 and 0.9. Where y is 0, the carbide is a binary carbide consisting essentially of carbon and M^1 having the formula ratio of M^1C_x. Where y is greater than 0 (e.g., between 0.1 and 0.9), the carbide is a ternary carbide consisting essentially of carbon, M^1, and M^2 having the formula ratio $M^1M^2_yC_x$.

As used herein, the term "article" includes nanorods, sheets, cages, shaped forms, and irregular crystalline or amorphous forms, such as dendritic or starburst forms. An article, such as a sheet, may be substantially planar, wavy, corrugated, or helical. An article may have one or more pores, grooves, or other textured topology.

As used herein, the term "nanorod" means a space-filling article with an aspect ratio of at least 10 (e.g., at least 50, at least 100, or at least 500). In general, the aspect ratio is between 25 and 1000, (e.g., between 100 and 1000, between 50 and 500, between 100 and 500, or between 500 and 1000). A nanorod has a shorter axis of between 0.1 and 80 nm (e.g., between 1 and 40 nm, and preferably between 2 and 30 nm). In other words, the length of a nanorod is between 0.02 and 50 μm, and preferably between 0.5 and 25 μm. The disclosed nanorods are solid, being neither hollow with one or two open ends, nor hollow with two sealed ends.

There may be impurities in or on the carbide lattice material such as oxygen (up to 10%), halogen (up to 2%), silicon (up to 5%), tellurium (up to 1%), and SP_2 hybridized carbon (up to 5%). The sources of these impurities are typically the reactants (metal oxide, transport molecules and transport agents) used in forming volatile metal and nonmetal species. These impurities are covalently bonded within the lattice, covalently bonded to or physically adsorbed to the surface of the nanorod, or located in interstitial sites (caged) within the lattice. In some embodiments, the presence of some impurities is desirable. For example, the presence of silicon is desirable to enhance or impart greater strength or fracture resistance for applications in

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intercombustion engines and gas turbines. It is believed that the term "consisting essentially of" allows for the above-described impurities.

As used herein, the term "short axis" is equivalent to "diameter," meaning the shortest dimension or cross-sectional thickness of a nanorod. Where a nanorod is, e.g., helical or networked, the diameter is always measured across the thickness of the rod, and not the overall diameter of the helix or the network, which is generally much greater than the diameter of the nanorod. In general, the diameter of a nanorod is substantially the same along the length of the nanorod. In some embodiments, a nanorod may have pores, grooves, or a fluctuating diameter (in an embodiments with a fluctuating diameter, the diameter is the average diameter).

As used herein, the term "length" means a longitudinal dimension (or approximation) of the nanorod that is orthogonal to the diameter of the nanorod. Length is not the overall size of a helix or overlapping network, which (if made of only one nanorod) is generally shorter than the length of the nanorod. If a helix or network is made of more than one nanorod, the length of a nanorod may be larger or smaller than the overall length of the helix or network.

DETAILED DESCRIPTION OF THE INVENTION

The invention is based, in part, on the discovery that carbon nanotubes are essentially completely converted to solid, covalently bound binary (or ternary) carbide nanorods. Conversion of nanotubes to carbide materials is essentially complete. In general, greater than 70% and typically 80% of the carbide materials are nanorods (having an aspect ratio of at least 10 and a diameter between 1 and 40 nm), the remaining 20% being carbide materials having aspect ratios less than 10, i.e., closer to particulates. Typically, the nanorod products have been shown to consist of at least 90% (and generally 95%) sp^3 hybridized carbon and the designated metal or nonmetal elements M^1 and M^2, the remaining 5–10% being impurities such as oxygen, silicon, halogen, or tellurium, or combinations thereof.

The disclosed nanorods have the formula ratio $M^1M^2_yC_x$, and a diameter of between 1 and 40 nm and an aspect ratio of between 10 and 1000. The diameter of the nanorods can be controlled in large part by the carbon nanotube precursor. In some embodiments that contain silicon, the diameter of the product increases slightly. This increase can be minimized by reducing reaction time.

Element M^1 is selected from the first element group consisting of titanium, silicon, niobium, iron, boron, tungsten, molybdenum, zirconium, hafnium, vanadium, tantalum, chromium, manganese, technetium, rhenium, osmium, cobalt, nickel, a lanthanide series element (i.e., cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium), scandium, yttrium, and lanthanum. Preferred M^1 are titanium, silicon, niobium, iron, boron, gadolinium, tungsten, molybdenum, zirconium, hafnium, vanadium, tantalum, and chromium.

Element M^2 is selected from the group consisting of nitrogen, boron, phosphorus, zinc, aluminum, copper, germanium, cadmium, indium, tin, lead, thallium, and the elements in the first element group (i.e., titanium, silicon, niobium, iron, boron, tungsten, molybdenum, gadolinium, zirconium, hafnium, vanadium, tantalum, chromium, manganese, technetium, rhenium, osmium, cobalt, nickel, cerium, praseodymium, neodymium, promethium,

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samarium, europium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, scandium, yttrium, and lanthanum). Preferred M^2 are selected from nitrogen and boron.

The ratio x of carbon to M^1 in a binary carbide (M^1C_x) or a ternary carbide ($M^1M^2_yC_x$) is between 0.1 to 2.1. Where M^1 is Ti, Zr, or Hf, x is preferably between 0.5 and 1.1, and more preferably between 0.9 and 1.1 (i.e., stoichiometric). Where M^1 is V, Nb, or Ta, x is preferably between 0.7 and 2.1. Other preferred ratios are as follows: Mo and W (0.6–2.1); Cr and Mn (0.2–0.7); Tc, Re, and Os (0.7–1.1); Fe, Co, and Ni (0.2–0.5); lanthanide elements such as Gd, Dy, and Yb (0.5–1); and B (0.1–0.3). The value for y is between 0 and 0.9, y being 0 in binary carbides. Stoichiometric carbide nanorods have enhanced conductivity and lower chemical reactivity, due to fewer carbon vacancies.

The properties of the disclosed, highly anisotropic nanorods are determined in numerous ways known to those in the art. These methods include transmission electron microscopy (TEM) to measure stacking fault density; energy-dispersive X-ray fluorescence to measure presence of nonmetals, metals, and impurities having a mass greater than or equal to sodium; electron energy loss spectroscopy to measure the hybridization of carbon; powder X-ray diffraction (XRD) to measure the crystal lattice structure; and convergent beam electron diffraction to measure lattice symmetry or the lattice constant a (Å).

The nanorods are also characterized by crystal structure (amorphous, polycrystalline, or single crystal). The crystal structure can be affected, in part, by the temperature and time of reaction. First, amorphous carbide materials are generally obtained at low reaction temperatures, e.g., below 1000° C. or even below 500° C. Second, polycrystalline materials are generally obtained under conditions where: (i) nucleation of the carbide occurs at multiple uncorrelated sites along the carbon reactant (e.g., nanotube) and (ii) there is insufficient energy or time for the uncorrelated crystalline domains to rearrange into a single crystal structure. Nevertheless, temperatures required to produce polycrystalline materials are always higher than temperatures required to produce an amorphous phase of the same carbide.

Third, single crystal materials are generally obtained when nucleation of the carbide occurs at a single site (e.g., an end of a carbon nanotube), and the growth of the carbide phase spreads outward from this single site. Alternatively, it is possible for a polycrystalline material to rearrange into a single crystal material at temperatures sufficiently high to promote diffusion and atomic rearrangement. A single crystal material consists of a single domain which may have few defects (high quality single crystal) or many defects (low quality single crystal). In general, the radial composition for single crystal nanorods are uniform; however, the invention encompasses nonuniform radial doping in nanorods. While essentially straight nanorods are preferred, the invention also encompasses straight, helical, crosslinked, and networked geometries made of one or more nanorods.

On the one hand, the disclosed articles generally retain the qualitative properties of the corresponding bulk carbide. For example, a NbC nanorod has superconductive properties, and a Fe_3C nanorod has magnetic properties (see Examples 3 and 5, respectively). On the other hand, compared with large carbide whiskers, the disclosed nanorods have a increased surface-to-volume ratio, which improves mechanical strength (e.g., tensile strength) and chemical reactivity.

Methods known in the art of measuring tensile strength are designed for existing fibers or whiskers, which are much

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larger than the disclosed nanorods. Therefore, a novel procedure is necessary for measuring the tensile strength of nanorods, such as using an atomic force microscope to apply known loads to a nanorod until it fractures or plastically deforms. A linear extrapolation based on T. Takahashi, *J. Electrochem. Soc.* 117:541 (1970) suggests that the tensile strength of nanorods is over ten times that of the corresponding whisker (10 microns in diameter), and possibly as much as 8000 times greater.

Synthesis

The nanorods disclosed herein are synthesized by the reaction of carbon nanotubes with a volatile metal or nonmetal species. In general, the reaction is carried out under static conditions in a sealed quartz tube with the reaction temperature dictated by the gas-phase transport of the oxide/ halide reactants and carbide growth (see Examples 1–5). The carbon nanotube reactants need not be anchored or tensed in any way to produce essentially straight nanorod products. Reaction temperatures are generally between 500 and 2500° C., and preferably between 600 and 1700° C. In general, the reaction can be monitored by measuring the conversion of carbon nanotube to carbide article and the structure of the carbide article.

The carbon nanotube reactants used in these vapor-solid reactions were obtained from metal-catalyzed growth using ethylene and hydrogen, adapted from C. E. Snyder et al. WO 89/07163 (1989), or are commercially available from Hyperion Catalysis International, Lexington Mass. This procedure yields relatively pure nanotube samples compared with arc-discharge methods, although some nanotubes exhibit poor crystallinity. Alternatively, nanotubes may be prepared by arc discharge procedures as described, for example, by S. Iijima, *Nature* 354:56–58 (1991), T. W. Ebbesen and P. M. Ajayan, *Nature* 358:220–222 (1992), and D. T. Colbert et al. *Science* 266:1218–1222 (1994).

In general, it is preferred to use nanotubes having fewer carbon defects. A defect includes any irregularity or nonstoichiometery in the crystal structure, such as a missing carbon atom (vacancy), a missing carbon—carbon bond (dislocation), or a stacking fault. Defects can be repaired or minimized by annealing the nanotubes in an inert (e.g., He or Ar) atmosphere at temperatures exceeding 1400° C. and preferably between 1400 and 2000° C. Annealing not only repairs defects but also improves both straightness and crystallinity of the graphitic nanotubes, which are generally highly curved.

Turning to the source of a metal or nonmetal, an important consideration is the volatility of the material under the chosen reaction conditions. A volatile metal or nonmetal oxide species (source of M^1, and M^2 if present) is obtained by combining commercially-available reagents selected from the group consisting of a pure metal or nonmetal, a metal or nonmetal oxide, a halogen transport molecule, and a halogen transport agent. At least one mole equivalent, and generally between 2 and 10 mole equivalents, of a metal or nonmetal reactant is used.

A carbon source (e.g., nanotube) is reacted with, for example, (i) a pure transition metal and a halogen transport molecule selected from the group consisting of I_2, Br_2, Cl_2 or a transport agent such as $TeCl_4$, or (ii) a metal or nonmetal oxide and a halogen transport agent to form a binary carbide. Ternary carbides are formed from two corresponding metal or nonmetal reagents, such as a pure metal or nonmetal, a halogen transport molecule, and a nitrogen source such as N_2 or NH_3. Transition metals are generally not sufficiently volatile under reaction conditions, but will form volatile complexes with the above-described halogen reagents. In

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addition, the transport agent $TeCl_4$ forms volatile species with most nonvolatile oxides, including MnO_2 and MoO_2. Some reactants are generated in situ, such as B_2O_2, which was generated in situ by heating elemental boron and TiO_2 powder. Specific examples of such reagents include TiO, I_2, B_2O_2, $FeCl_3$, and SiO. Additional examples and guidance are found in H. Schafer, *Angew. Chem. Int. Ed., Engl.* 10:43–50 (1971). Commercially-available reagents generally do not require pre-treatment before use, since their purity is typically ≧99%. Commercial sources include Aldrich Chemicals, Milwaukee, Wis., and Johnson-Mathey, Ward Hill, Mass.

Examples of binary carbides include ZrC_x, HfC_x, VC_x, TaC_x, CrC_x, MoC_x, WC_x, and NiC_x (formed, e.g., by reaction of pure metal and halogen transport molecule with a carbon source); and LaC_x, CeC_x, PrC_x, NdC_x, SmC_x, GdC_x, DyC_x, HoC_x, ErC_x, and YbC_x (formed, e.g., by reaction of metal oxide and halogen transport agent with a carbon source). Examples of ternary carbides include TiN_yC_x, MoN_yC_x, and SiN_yC_x (formed, e.g., by reaction of pure metal/nonmetal, halogen transport molecule, and nitrogen or ammonia with a carbon source); TiB_yC_x, $TiTa_yC_x$, $TiSi_yC_x$, $TiNb_yC_x$, $MoSi_yC_x$, MoB_yC_x, $MoGa_yC_x$, $MoAl_yC_x$, FeB_yC_x, $FeSi_yC_x$, $FeNi_yC_x$, SiB_yC_x, $TaSi_yC_x$, WSi_yC_x, $ZrSi_yC_x$, $NbSi_yC_x$, $CrSi_yC_x$, and WCo_yC_x (formed, e.g., by reaction of metal and halogen transport molecule with a carbon source); and $MoSi_yC_x$, WSi_yC_x, $ZrSi_yC_x$, $NbSi_yC_x$, $CrSi_yC_x$, WCo_yC_x, NdB_yC_x and $FeNd_yC_x$ (formed, e.g., by reaction of metal oxide and halogen transport agent with a carbon source).

Without intending to be bound, it is believed that the mechanism involves template-mediated growth, whereby carbon nanotubes define the diameter of the product carbide nanorods formed following reaction with a volatile species. This is supported by the similarity of the average nanorod diameters (and morphologies in the case of polycrystalline NbC) to that of the starting nanotubes. Catalytic growth and/or sintering of small nanotubes may also be involved. In principle, template mediated growth will produce carbide nanorods of any stable metal carbide.

Solid carbide nanorods (SiC, TiC, NbC, Fe_3C, and BC_x) have been prepared in high-yield with typical diameters between 2 and 30 nm and lengths up to 20 μm (see Examples 1–5 below).

Use

The disclosed nanoscale articles are used in the preparation of nanostructures having a superior combination of a uniquely small size and mechanical, electrical and/or magnetic properties, suitable for electrodes in nanoscale batteries and for high density magnetic recording media. Small diameters and high aspect ratios also make the disclosed articles useful as improved reinforcements in metal, ceramic, and organic polymer matrix composites. A carbide article disclosed herein can be selected from a wide range of metal and nonmetal carbides to suit the chemical properties (e.g., resistance, reactivity) or physical properties (e.g., coefficient of thermal expansion) desired for a particular composite. Specific products include cutting tools, engineering composites such as gas turbine blades and automotive ceramics, and implantable medical devices such as artificial limbs and joints. Conductive or semi-conductive nanorods are also useful as "defects" embedded within a superconductor to pin vortices in high-temperature, high critical current density superconductor wires (e.g. copper oxide), see P. Le Doussal and D. R. Nelson, *Physica C* 232:69–74 (1994). Finally, the disclosed nanoscale articles are used in basic research to probe the effects of confinement and dimensionality in metallic, semiconducting and superconducting materials.

Without further elaboration, it is believed that one skilled in the art can, based on the description herein, utilize the present invention to its fullest extent. All patents and publications cited herein are hereby incorporated by reference. The following specific examples are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure.

EXAMPLES

Example 1

Titanium carbide nanorods were made according to two different methods, Method A and Method B.

Method A. The starting mixture was composed of 20 mg of carbon nanotubes produced as described above, and a compacted, solid pellet consisting of a 10-fold molar excess of TiO powder. After sealing the starting mixture under vacuum (1×10^{-3} torr) in a quartz tube, the tube was placed in the center of a tube furnace equilibrated at a temperature of 1350° C. for 12 hours. Then the furnace was turned off and allowed to cool naturally to room temperature. After removing the quartz tube from the furnace and opening it to the atmosphere, the unreacted TiO powder, still in pellet form, was manually removed from the black nanorod product, which had a fine, powder-like consistency. The nanorods were poured from the quartz tube and thoroughly washed with ethanol and dried in air.

Method B. In the second method, the same procedure described in Method A was followed, except an amount of solid iodine corresponding to 1 mg I_2 per cm^3 of the quartz reaction tube was added to the tube, and the quartz tube was heated at 1200° C. for 24 hours.

The morphology and structure of the products obtained from the reaction of TiO and carbon nanotubes at 1375° C. were determined. Transmission electron microscopy (TEM) images of the reaction product revealed straight and smoothly curved, solid rod-like structures that were distinct from the irregularly curved and hollow carbon nanotube reactants. These images also showed that the diameters of the rod-like products were similar to that of the carbon nanotubes (1–30 nm), and that the lengths typically exceeded 1 μm and were measured up to 40 μm. Energy dispersive X-ray fluorescence and electron energy loss spectroscopy measurements demonstrated that these nanorods contained only titanium and sp^3-hybridized carbon, and thus are consistent with the complete conversion of the carbon nanotubes into titanium carbide (TiC).

This formulation was further established by structural analyses. Powder X-ray diffraction (XRD) measurements on nanorod samples produced using either TiO or Ti+I_2 exhibited diffraction peaks that were indexed to the known cubic, rock salt structure of TiC with no evidence of either graphitic (nanotube reactant), Ti-metal or Ti-oxide peaks present. The measured lattice constant, a=4.326 Å, was consistent with a stoichiometry TiC$_x$, x=1. TEM and electron diffraction studies of single nanorods revealed smooth, regular saw-tooth, and irregularly faceted morphologies. The TiC nanorods also appeared to be single crystals with a very low density of stacking faults. Convergent beam electron diffraction patterns recorded along the <111> zone axis perpendicular to the axis of the smooth nanorod exhibited a lattice constant and six-fold symmetry corresponding to the (111) planes of cubic TiC. These data suggested that the axis of the smooth TiC nanorods was [110] for this morphology as well. The [110] direction is not unique for the TiC nanorods. In the irregularly faceted nanorods, high-resolution TEM and elec-

tron diffraction demonstrated that the growth direction was [111], and further showed that the TiC nanorods contained single crystal domains often exceeding 1 μm in length. The saw-tooth morphology has obvious advantages for some applications (e.g., composites).

Example 2

SiC nanorods were synthesized according to two methods. In the first, the same procedure described in Method A, Example 1 was followed, except SiO powder was substituted for TiO powder, and the quartz tube was heated at 1300–1400° C. for 2 hours, then cooled to room temperature over an additional 2 hours. The silicon carbide nanorod product was blue-green.

In the second, the same procedure described in Method B, Example 1 was followed, except SiO powder was substituted for TiO powder and the quartz tube was heated at 1150° C. for 2 hours. Structural and composition analyses of the material produced from the reaction of carbon nanotubes with Si and I_2 were consistent with the formation of silicon carbide (SiC) nanorods. TEM images showed that the SiC nanorods produced from this reaction were relatively straight, solid rods. The diameters of the SiC rods produced in the Si+I_2 reaction at 1200° C. were typically 2–20 nm (similar to the diameters of the carbon nanotube reactants), with lengths around 1 μm. XRD patterns recorded on bulk samples were indexed to the zinc blended β-SiC structure and showed no evidence of other crystalline impurities. TEM images and electron diffraction data also indicated that these single crystal silicon carbide nanorods possessed a higher density of planar defects in contrast to the near single crystal TiC nanorods (see Example 1 above). For SiC nanorods with a [111] rod axis, the defects corresponded to rotational twin stacking faults; similar defects have been identified previously in much larger SiC whiskers. The rod axes lay along the [111] direction in all of the nanorods prepared at 1300–1400° C. using SiO as the volatile silicon reactant, but at the lower Si+I_2 reaction temperatures (1100–1200° C.) this direction was not unique. A high-resolution TEM image of one 7 nm diameter SiC nanorod produced at 1200° C. showed that the rod axis lay along the [100] direction, although small defect regions with a [111] direction were also present.

Example 3

Twenty milligrams of carbon nanotubes and a 10-fold molar excess of pelleted elemental niobium powder were sealed under vacuum (1×10^{-3} torr) with an amount of iodine corresponding to 1 mg/cm^3 volume of the quartz reaction tube. The tube was placed in the center of a tube furnace equilibrated at 750° C. for 35 hours, then cooled to room temperature in 30 minutes. The quartz tube was opened to atmosphere, and the remaining unreacted Nb was removed in pellet form. The black nanorod product was poured from the quartz reaction tube, washed thoroughly with ethanol, and then dried.

XRD showed that this reaction resulted in the complete conversion of the nanotubes into the cubic, rock salt phase of NbC. TEM images and selected area electron diffraction showed that the NbC nanorods produced in these reactions were polycrystalline with morphologies similar to the carbon nanotube starting materials. Significantly, these polycrystalline nanorods were also found to be superconducting like bulk NbC, as shown by magnetization measurements made as a function of temperature (T_c=9° K.). The polycrystalline structure was likely due to the low reaction

temperature (750° C.), and thus it should be possible in the future to optimize the growth conditions and produce single crystal NbC nanorods by raising the reaction temperature. The present reaction conditions also yielded unique morphologies, such as helical nanorods, which are believed to result from a direct conversion of helical carbon nanotube reactants. The NbC nanorods had diameters of between 2 and 30 nm, and lengths generally greater than 1 micron.

Example 4

Twenty milligrams of carbon nanotubes and a 10-fold molar excess of anhydrous $FeCl_3$ powder were sealed under vacuum (1×10^{-3} torr). The tube was placed in the center of a tube furnace equilibrated at 1350° C. for 12 hours, then cooled to room temperature in 2 hours. The quartz tube was opened to atmosphere, and the remaining unreacted $FeCl_3$ was removed from the black nanorod product by repeated washing with ethanol. The black Fe_3C nanorod product was poured from the quartz reaction tube was dried in air.

TEM analysis demonstrated that the solid, amorphous nanorods consisted of covalently bonded Fe and C. Magnetization measurements showed that the iron carbide nanorods were ferromagnetic. The iron carbide nanorods had diameters of between 2 and 30 nm, and lengths generally greater than 1 micron.

Example 5

Elemental boron powder and titanium dioxide powder were mixed thoroughly in a 1:1 molar ratio and placed in a crucible boat in an amount equivalent to a 10-fold molar excess relative to 20 mg of carbon nanotubes. Twenty milligrams of carbon nanotubes and the B-TiO_2 mixture were separately placed in a horizontal quartz tube open at both ends, and in turn, the horizontal quartz tube was placed in a horizontal tube furnace. The end of the quartz tube nearest to the B-TiO_2 mixture was fitted with a gas inlet through which argon gas was slowly flowed. The other end of the quartz tube (nearest to the nanotubes) was fitted with a flexible tube connected to a bubbler. The argon flow was adjusted to produce about 1 bubble/second.

After flowing argon through the quartz tube for 30 minutes to purge atmospheric gases, the furnace temperature was increased to 1400° C. over a period of 1 hour. The furnace was maintained at 1400° C. for 2 hours, turned off, and allowed to cool naturally to room temperature. The quartz tube was opened to atmosphere, and the remaining unreacted B-TiO_2 was removed in the crucible boat. The black nanorod product was poured from the reaction tube, washed thoroughly with ethanol, and dried.

Analysis showed the solid nanorods consisted of polycrystalline, covalently bonded boron and carbon. The boron carbide nanorods had diameters of between 2 and 30 nm, and lengths generally greater than 1 micron. In addition, the nanorods were shown to have insulating properties. Using a scanning probe microscope and modified lithography techniques, a single nanorod was contacted on one end with a gold electrode. A second movable probe electrode was contacted with the single nanorod at different points, and conductivity was measured.

OTHER EMBODIMENTS

From the above description, the essential characteristics of the present invention can be ascertained. Without departing from the spirit and scope thereof, various changes and modifications of the invention can be made to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

What is claimed is:

1. A carbide nanorod consisting essentially of TiC, NbC, Fe_3C, or BC_x in which x is between 0.1 and 2.1, inclusive, wherein said nanorod has an aspect ratio of between 11 and 1000, and has a shorter axis of between 1 and 40 nanometers.

2. A carbide nanorod consisting essentially of covalently bonded elements M^1, M^2 and C having the molar ratio $M^1{:}M^2{:}C{::}1{:}y{:}x$,

wherein said first element M^1 is tungsten, molybdenum, zirconium, hafnium, vanadium, tantalum, chromium, manganese, technetium, rhenium, osmium, cobalt, nickel, a lanthanide series element, scandium, yttrium, or lanthanum;

said second element M^2 is nitrogen, boron, phosphorus, zinc, aluminum, copper, germanium, cadmium, indium, tin, lead, thallium, or the elements in said first element group, in which y is between 0 and 0.9, inclusive, provided that said first and second element are not the same; and

said third element C is carbon, in which x is between 0.1 and 2.1, inclusive;

wherein said nanorod has an aspect ratio of between 11 and 1000, and has a shorter axis of between 1 and 40 nanometers.

*   *   *   *   *

United States Patent [19]

Moskovits et al.

[11] **Patent Number:** **6,129,901**

[45] **Date of Patent:** **Oct. 10, 2000**

[54] **CONTROLLED SYNTHESIS AND METAL-FILLING OF ALIGNED CARBON NANOTUBES**

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[73] Assignees: **Martin Moskovits; Jing Li; Thomas Haslett**, all of Toronto, Canada

[21] Appl. No.: **09/186,092**

[22] Filed: **Nov. 5, 1998**

Related U.S. Application Data

[60] Provisional application No. 60/065,692, Nov. 18, 1997.

[51] Int. Cl.[7] D01F 9/127
[52] U.S. Cl. 423/447.3; 423/439; 423/447.5
[58] Field of Search .... 423/447.3, 447.2, 423/445 B, 447.5, 439

[56] **References Cited**

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Primary Examiner—Steven Bos
Assistant Examiner—Peter DiMauro
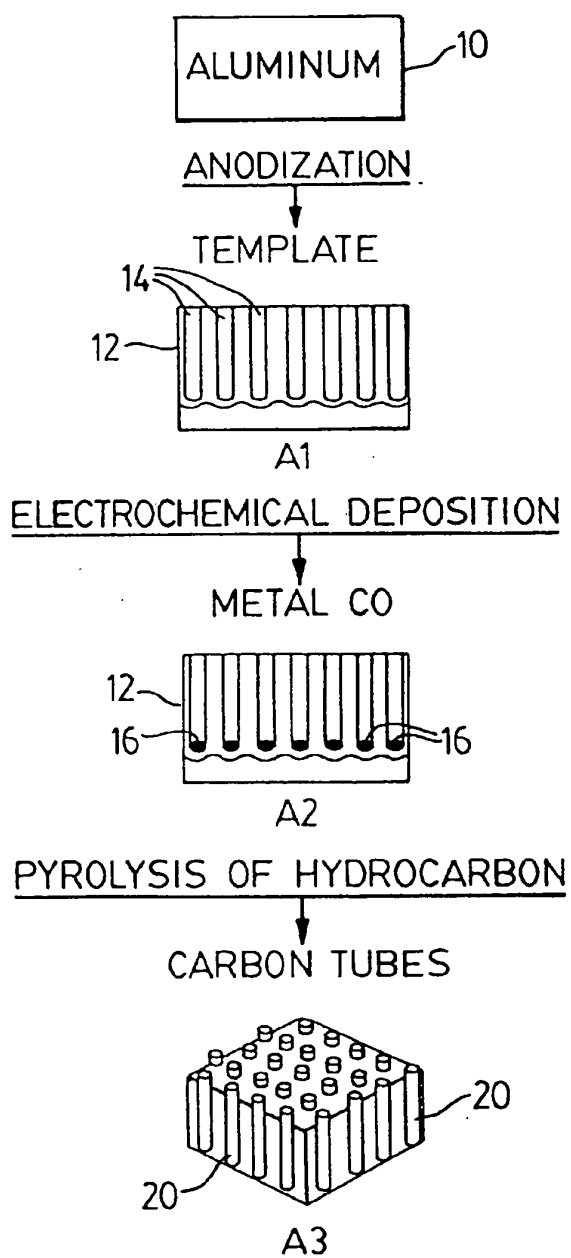*Attorney, Agent, or Firm*—Lynn C. Schumacher; Hill & Schumacher

[57] **ABSTRACT**

The present invention provides a powerful new method for producing, uniform sized and uniformly aligned nanotubes through catalytic pyrolysis of a hydrocarbon within the dense, uniform and parallel pores of alumina nano-templates. The catalyst, Co, Fe, Ni or another suitable substance is deposited electrochemically into the bottom of the channel of the alumina template. The nanotubes with any desired diameter in the range 5–500 nm and lengths up to ~100 μm, are generated by the pyrolysis of a suitable hydrocarbon inside the pores of the alumina template with at least one end open at the alumina/air interface. The nanotubes may be filled by metals using for example electroless deposition.

23 Claims, 5 Drawing Sheets

ALUMINUM ⌐10

ANODIZATION

14 ⎺TEMPLATE

12⌐

A1

ELECTROCHEMICAL DEPOSITION

METAL CO

12⌐
16⌐ ⌐16

A2

PYROLYSIS OF HYDROCARBON

CARBON TUBES

20

20

A3
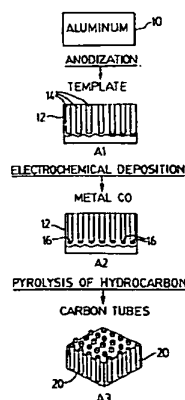
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ALUMINUM ─10

ANODIZATION

TEMPLATE

14

12

A1

ELECTROCHEMICAL DEPOSITION

METAL CO

12

16 ─── ───16

A2

PYROLYSIS OF HYDROCARBON

CARBON TUBES

20

20

A3

FIG. 1
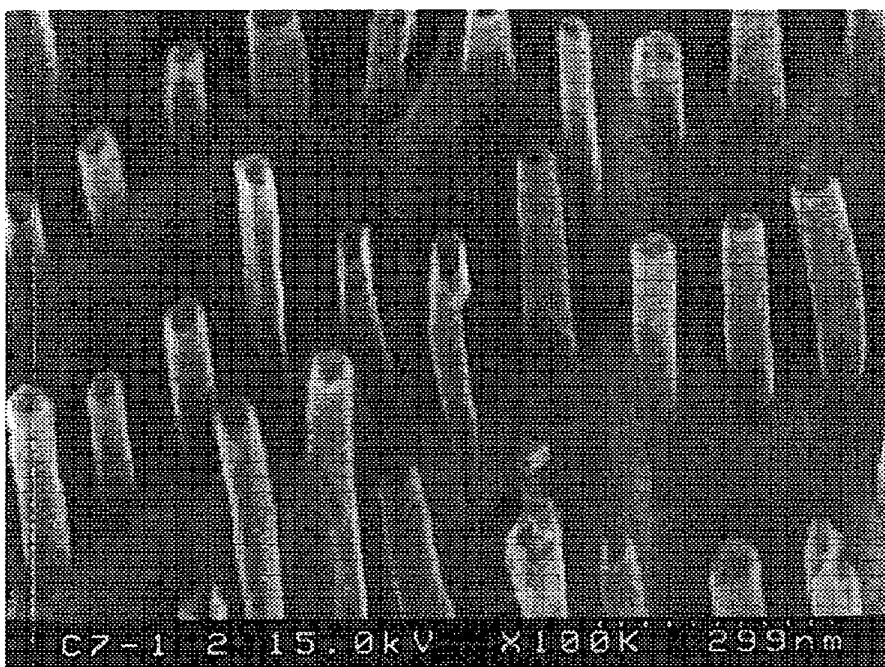
FIG. 2

SEM image of exposed carbon nanotubes after etching partially away template surface by NaOH solution.
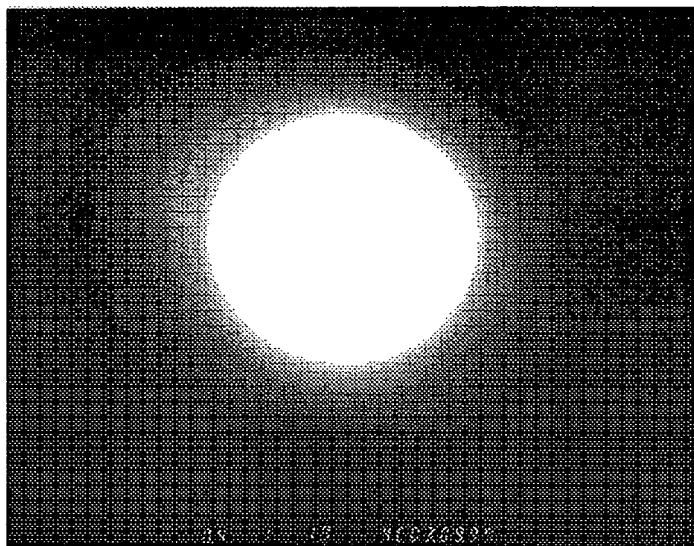
FIG. 3a

Electron diffraction pattern of carbon nanotubes
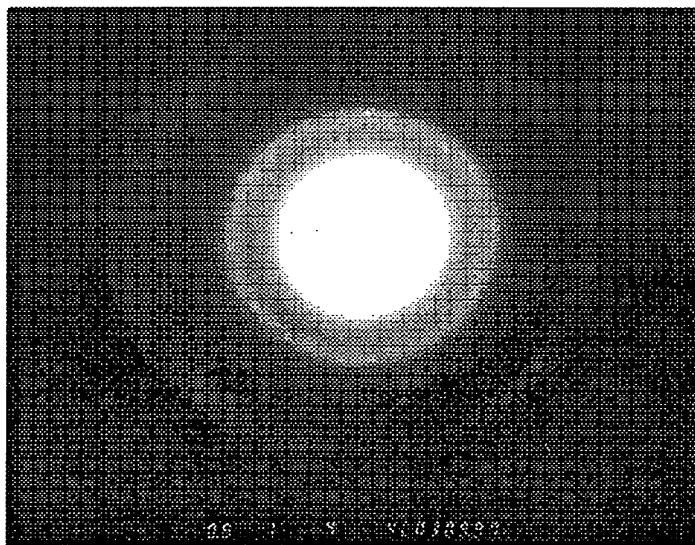
FIG. 3b

Electron diffraction pattern of nickel filled carbon nanotubes
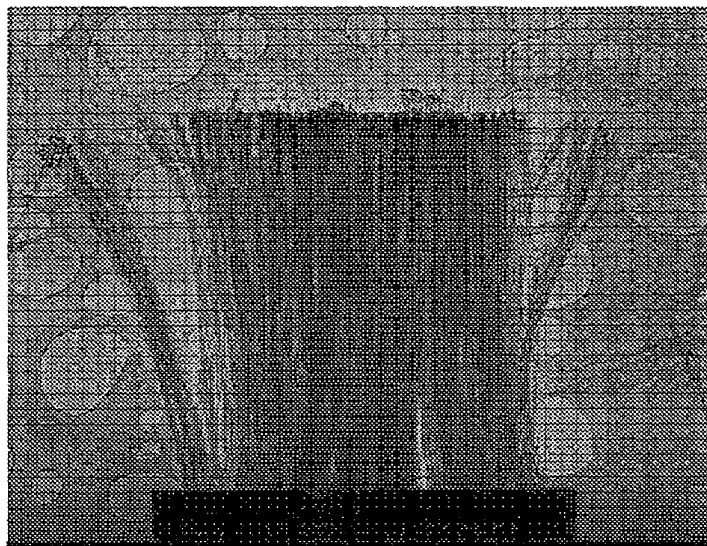
FIG. 4a

TEM images of carbon nanotubes
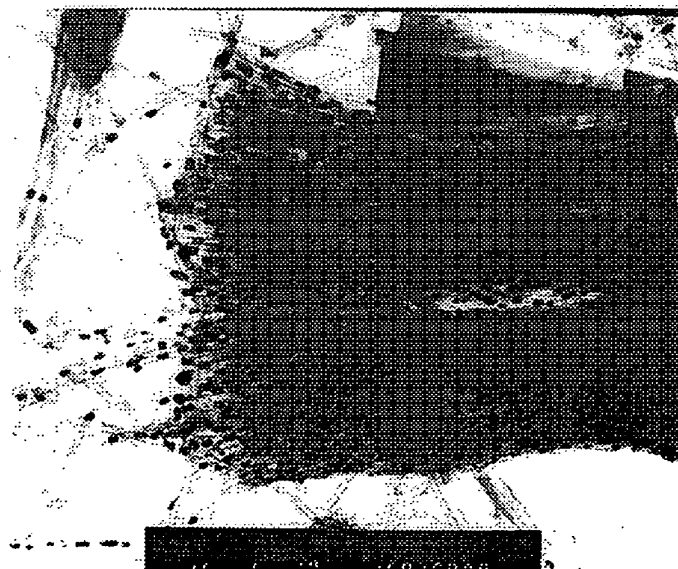
FIG. 4b

TEM images of nickel filled carbon nanotubes
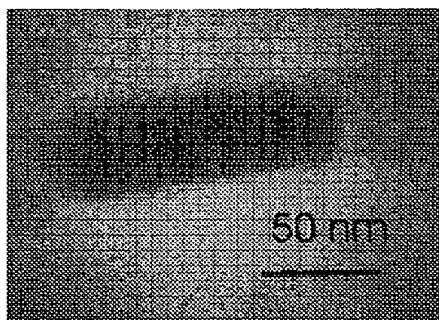
FIG. 5a
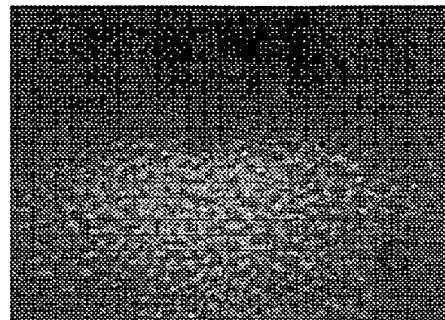
FIG. 5b
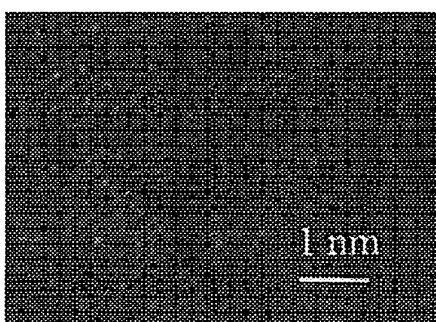
FIG. 5c

FIG. 5d

TEM images of a) Ni–P alloy encapsulated within the carbon nanotubes, b, d) High resolution images of the interface of Ni–P alloy and carbon, and c) Ni–p alloy

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CONTROLLED SYNTHESIS AND METAL-FILLING OF ALIGNED CARBON NANOTUBES

CROSS REFERENCE TO RELATED UNITED STATES PATENT APPLICATION

This patent application relates to United States Provisional Application Serial No. 60/065,692 filed on Nov. 18, 1997, entitled CONTROLLED SYNTHESIS AND METAL-FILLING OF ALIGNED CARBON NANO-TUBES.

FIELD OF THE INVENTION

The present invention relates to a method of synthesis of aligned carbon nanotubes through catalytic pyrolysis of hydrocarbon within alumina nano-templates. The present invention also relates to a method of filling the inner cavity of the nanotubes with metals and more particularly the method relates to electroless plating of metals including but not limited to Ni, Co, their alloys and other metals into the inner cavity of the nanotubes and filling the metals inside.

BACKGROUND OF THE INVENTION

Carbon nanotube, a novel carbon material, was theoretically predicted and experimentally shown to possess unique electronic and mechanical properties and is of great scientific and potential commercial value. Recent studies reveal that the diameter, number of concentric cylinders and helicity of the arrangement of the carbon atoms in the nanotube shell determine whether the nanotube has metallic, semiconducting or insulating properties. Hence a wide range of materials properties may be "tuned in" by changing the structural properties of these nanotubes. The stiffness and high strength of these carbon nanotubes make them ideal probes in scanning probe microscopy, and efficient field-emitters, as recently shown by Smalley's group. Additionally the inner hollow cavity of the nanotubes may serve as nanometer scale test tubes in which to carry out interesting experiments with submicroscopic quantities of reagents. Nanotubes filled with metallic or semiconducting particles might serve as the constituents of novel materials with useful magnetic, electrical or electronic properties leading to new devices.

The conventional synthesis methods for carbon nanotube include carbon arc discharge (S. Iijima, *Nature*, 354, 56, 1991) and catalytic pyrolysis of hydrocarbon (M. Endo, K. Takeuchi, S. Igarashi, K. Kobori, M. Shiraishi, H. W. Kroto, *J. Phys. Chem. Solids*, 54, 1841, 1993), which generate nanotubes often containing traces of the catalyst particles used to generate them and possessing highly variable dimensions. Synthesis of aligned nanotube by pyrolysis of hydrocarbon with a patterned cobalt catalyst on silica substrate was recently reported by M. Terrones et al, *Nature*, 388, 52, 1997 and with iron nanoparticles in mesoporous silica by W. Z. Li et al, *Science*, 274, 1701, 1996. The successful production of carbon nanotubes in an alumina template by pyrolysis of propylene has been disclosed by T. Kyotani, L. Tsai, A. Tomita, *Chem. Mater.*, 8, 2190, 1996.

The encapsulation of foreign materials in the carbon nanotubes has been disclosed by P. M. Ajayan and S. Iijima (U.S. Pat. No. 5,457,343). Ni, Fe, Co, rare earth metals and their carbides were found to be encapsulated in the nanotubes during synthesis of them in carbon arc discharge by Y. Saito et al, *J. Phys. Chem. Solids*, 54, 1849, 1993, and also by C. Guerret-Piecout et al, *Nature*, 372, 761, 1994. The

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metals with a low melting point, such as lead, zinc, selenium, and molten metal salt, $AgNO_3$ were filled through capillarity into the carbon nanotubes, reported by P. M. Ajayan et al, *Nature*, 362, 522, 1993, E. Dujardin et al, *Science* 265, 1850, 1994 and by D. Ugarte et al, *Science*, 274, 1897, 1996.

SUMMARY OF THE INVENTION

It is an object of the present to provide a method of producing carbon nanotubes of uniform size and uniformly aligned in the axial direction.

The present invention provides a powerful new method for producing, uniform sized and uniformly aligned nanotubes through catalytic pyrolysis of a hydrocarbon within the dense, uniform and parallel pores of alumina nano-emplates. The catalyst, Co, Fe, Ni or another suitable substance is deposited electrochemically into the bottom of the channel of the alumina template. The nanotubes with any desired diameter in the range 5–500 nm and lengths up to ~100 μm, are generated by the pyrolysis of a suitable hydrocarbon inside the pores of the alumina template with at least one end open at the alumina/air interface.

The present invention provides a process for filling the carbon nanotubes obtained by above method with metal Ni, Co, Fe, Ag and their alloys by electroless (chemical) plating.

In one aspect of the invention there is provided a process for synthesis of carbon nanotube. The method comprises anodizing an aluminum substrate in an effective bath to produce an alumina template with a plurality of pores each having a pore diameter. The method includes depositing an effective catalyst into the pores and exposing the alumina template with the catalyst containing pores to an effective hydrocarbon gas at an effective temperature to grow carbon nanotubes in the pores. Each carbon nanotube has an outer diameter not greater than to the pore diameter in the template in which the carbon nanotube is produced.

In another aspect of the invention there is provided a process for producing metal containing carbon nanotubes, comprising:

a process for producing metal containing carbon nanotubes, comprising:

anodizing an aluminum substrate in an effective bath to produce an alumina template with a plurality of pores each having a pore diameter;

depositing an effective catalyst into the bottom of the pores; exposing the alumina template with the catalyst containing pores to an effective hydrocarbon gas at an effective temperature to grow carbon nanotubes in the pores, each carbon nanotube having an outer diameter not greater than to the pore diameter in the template in which the carbon nanotube is produced; and

depositing a metal into the nanotubes.

In this aspect of the invention the metal may be deposited into the nanotube by electroless deposition.

BRIEF DESCRIPTION OF THE DRAWINGS

The process of growth of carbon nanotubes and metal filling of the nanotubes will now be described, by way of example only, reference being had to the accompanying drawings, in which:

FIG. 1 is a schematic diagram showing the steps of synthesising carbon nanotubes in accordance with the present invention;

FIG. 2 is a scanning electron micrograph (SEM) of exposed carbon nanotubes after etching partially away the template surface in an NaOH solution;

FIG. 3a shows an electron diffraction pattern of carbon nanotubes produced according to the present invention;

FIG. 3b shows an electron diffraction pattern of nickel filled carbon nanotubes;

FIG. 4a shows a transmission electron micrograph (TEM) of carbon nanotubes produced by the present method;

FIG. 4b shows a TEM of nickel filled carbon nanotubes;

FIG. 5a shows transmission electron micrographs of Ni-P alloy encapsulated within the carbon nanotubes;

FIGS. 5b and 5d show high resolution images of the interface of Ni-P alloy and carbon; and

FIG. 5c shows a high resolution TEM of Ni-P alloy.

DETAILED DESCRIPTION OF THE INVENTION

The process of synthesizing carbon nanotubes is showed schematically in FIG. 1. Anodic oxidation of an aluminum (99.99%) substrate 10 was carried out in 0.3 M of oxalic acid bath at cell voltages of 25, 40, 50 and 65 V respectively at 18° C. While the oxalic acid bath is preferred, other anodizing electrolyte media such as sulphuric, phosphoric and chromic acids may also be used. In these examples the film thickness was controlled to lie in the range 4–10 μm by selecting the anodic oxidation time appropriately. Under the present experimental conditions, the film thickness is calculated using the formula: D=αltl/A; where a is an experimentally determined constant equal to 0.017 μm/(mA cm^{-2} min); / is the anodizing current in mA; t is the anodizing time in minutes, and A is the aluminum sample area in cm^2. Films in the range 1–100 μm may be generated in this way. The anodized alumina templates 12 were immersed in 0.1 M phosphoric acid at 30° for 30 min. to widen the pores and to thin the barrier layer. After widening, the average pore diameter of the pores 14 in template 12 obtained at cell voltages of 25, 40, 50 and 65 V are 20, 35, 50 and 70 nm, respectively. The pores 14 are straight, uniform and parallel as shown in the diagrammatic representation in FIG. 1.

A cobalt (or iron) catalyst sample 16 approximately 200 nm in length was electrochemically deposited at the bottom of the pores using 14 V and 100 Hz of AC cell voltage for 30 seconds in a bath consisting of 240 g/l of CoSO$_4$·7H$_2$O, (or 120 g/l of FeSO$_4$·7H$_2$O) 40 g/l of HBO$_3$ and 1 g/l of ascorbic acid. The cobalt-containing templates 12 were placed in a tube furnace and reduced at 600° C. for 4–5 hours in flowing CO (100 ml/min). Then a mixture of 10% acetylene in nitrogen was introduced into the reactor at a flow rate of 100 ml/min. Acetylene was decomposed by pyrolysis in the temperature range 640° C. to 700° C. to form the carbon nanotubes 20 in the template channels. While this is a preferred temperature range the acetylene may be decomposed in a range from 600° C. to about 800° C. In addition to acetylene, it will be understood that other hydrocarbon containing gases may be used, for example propylene and methane to mention just a few.

After formation, the nanotubes 20 were annealed to further graphitize the tubes at 700° C. in flowing nitrogen for 15 hours. FIG. 2 shows SEM image of the nanotubes whose ends were exposed by partially etching the alumina template with a NaOH solution. The nanotubes 20 are perpendicular to the template 12. Their ends at the alumina/air interface are open and their outer diameters correspond to the inner diameters of the pores 14. An electron diffraction pattern (FIG. 3a) recorded for a bundle of the nanotubes that had been released from the alumina template by dissolving the latter in a NaOH solution, (FIG. 4a) reveals an ordered

graphitic arrangement within the bundles. The inter-layer spacing in the 002 direction (d$_{002}$) deduced from the electron diffraction data is approximately 3.45 nm, which is close that value in graphite (d$_{002}$=3.35 nm).

Electroless nickel deposits were produced in an acid bath consisting of 30 g/l of nickel chloride, 10 g/l of sodium hypophosphite, 50 g/l of sodium acetate and ammonia to pH=5. The alumina templates containing carbon nanotubes were washed with acetone then with distilled water. The washed templates were dipped in the electroless deposition bath for 20–30 min at 25–40° C. The reaction producing the nickel deposit can be formulated as:

$$3NaH_2PO_2 + 3H_2O + NiCl_2 \rightarrow 3NaH_2PO_3 + 2HCl + 2H_2 + Ni^*$$
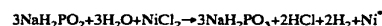
It was found that addition of 0.5 g/l of quinhydrone improved the deposition. The quinhydrone may function as a surfactant to increase the wetting of the walls of nanotubes by the solution and as a pH stabilizing agent. Other surfactants, such as gelatine, Dodecyl sulfate sodium salt, are also anticipated to improve the wetting efficacy of the deposition solution. After completely dissolving the alumina template using 0.1 M NaOH solution at 60–80° C., the metal-containing nanotubes (FIG. 4b) could be separated as an insoluble precipitate. An electron diffraction pattern (FIG. 3b) recorded for the bundle of nickel-containing nanotubes exhibits clear diffraction spots corresponding to Nickel metal, which coincidentally almost overlaps the diffraction rings produced by the carbon layers of the nanotubes due to the near-correspondence of some of the lattice constants. A lattice constant of approximately 3.52 nm is obtained from the electron diffraction pattern of the deposited metal. The high-resolution TEM image (FIG. 5) shows that the deposited metal is highly crystalline. An EDX analysis of the metal encapsulated in the nanotubes shows it to be a nickel/phosphorous mixture with an average Ni/P ratio of 94% Ni and 6% P.

While nickel, cobalt and iron are preferred catalysts for deposition into the pores of the anodized aluminum template for growth of the carbon nanotubes, it is anticipated by the inventors that other suitable or effective catalysts may be used. For example, the metals below each of these three preferred metals are reasonably expected to work to some degree.

Similarly, those skilled in the art will appreciate that numerous other metals may be deposited into the carbon nanotubes once formed. Examples include metals such as Ag, Cu, Bi, Pb and Sn may be deposited into the nanotubes by electroless deposition. It will also be understood by those skilled in the art that the nanotubes may be filled with the metals by electrochemical deposition.

The present method is highly advantageous over prior art methods of growing carbon tubes since in prior art methods the lack of catalyst in the pores yields tubes that exhibit poor uniformity along the tube axis due to the influence of diffusion of the gaseous reagents into and out of the pores of the template.

In the present method, it is not necessary to strip off the oxide film from the aluminum plate so that a thin film, i.e. a film that is not self-supporting, can also be used as a template allowing one to make tubes of any desired length, by using templates of the appropriate thickness in the practical range 0.1 μm to over 100 μm, in contrast to the method described by Kyotani et al. (Chem. Mater., 8,2190, 1996), that requires self-supporting templates and hence is incapable of making tubes below a minimum length below which the template is no longer self-supporting. The present method also provides a much more economical method of

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growing nanotubes since the number of procedural steps is decreased. The carbon nanotubes resulting from catalytic, thermal decomposition result in the growth of much more uniform tubes in the pores in contrast to tubes grown in templates without catalyst.

The foregoing description of the preferred embodiments of the process for producing carbon nanotubes has been presented to illustrate the principles of the invention and not to limit the invention to the particular embodiments disclosed. It is intended that the scope of the invention be defined by all of the embodiments encompassed within the following claims and their equivalents.

We claim:

1. A process for synthesis of carbon nanotubes, comprising:

    anodizing an aluminum substrate in an effective bath to produce an alumina template with a plurality of pores each having a pore diameter;

    depositing an effective catalyst into the pores; and

    exposing said alumina template with the catalyst containing pores to an effective hydrocarbon gas at an effective temperature to grow carbon nanotubes in said pores, each carbon nanotube having an outer diameter not greater than the pore diameter in the template in which said carbon nanotube is produced.

2. The process according to claim 1 wherein the aluminum substrate is anodized under conditions effective to produce said plurality of pores substantially parallel to each other.

3. The process according to claim 2 wherein said aluminum substrate is anodized in an effective acid bath.

4. The process according to claim 3 wherein said catalyst is selected from the group consisting of Co, Fe, Ni and alloys thereof.

5. The process according to claim 4 wherein said catalysts are electrochemically deposited into said pores.

6. The process according to claim 5 wherein said hydrocarbon gas comprises acetylene.

7. The process according to claim 6 wherein said hydrocarbon gas is pyrolized in a temperature range from about 600° C. to about 800° C.

8. The process according to claim 7 wherein subsequent to producing said carbon nanotubes, said carbon nanotubes are annealed to further graphitize said nanotubes.

9. The process according to claim 8 including depositing a metal into said nanotubes.

10. The process according to claim 9 wherein said metal deposited into said nanotubes is selected from the group consisting of Ni, Fe, Co and Ag.

11. The process according to claim 10 wherein said metal is deposited into said nanotubes by electroless deposition from an effective electroless deposition bath.

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12. The process according to claim 10 wherein said metal is deposited into said nanotubes by electrochemical deposition.

13. The process according to claim 11 wherein said electroless deposition bath comprises a surfactant selected from the group consisting of quinhydrone, gelatine and dodecyl sulfate sodium salts as additives for improving the electroless deposition of said metal.

14. The process according to claim 2 including immersing the alumina substrate in an effective solution to widen said pores and thin an alumina barrier layer on the interior surface of said pores.

15. The process according to claim 11 wherein said nanotubes are washed prior to electroless deposition of said metals.

16. The process according to claim 9 including dissolving the alumina template to separate the carbon nanotubes from said template.

17. The process according to claim 16 wherein said alumina template is dissolved in an NaOH solution.

18. The process according to claim 17 wherein the metal-containing nanotubes are separated as an insoluble precipitate.

19. A process for producing metal containing carbon nanotubes, comprising:

    anodizing an aluminum substrate in an effective bath to produce an alumina template with a plurality of pores each having a pore diameter;

    depositing an effective catalyst into the bottom of the pores;

    exposing said alumina template with the catalyst containing pores to an effective hydrocarbon gas at an effective temperature to grow carbon nanotubes in said pores, each carbon nanotube having an outer diameter not greater than the pore diameter in the template in which said carbon nanotube is produced; and

    depositing a metal into said nanotubes.

20. The process according to claim 19 wherein said metal is deposited into said nanotube by electroless deposition.

21. The process according to claim 20 wherein said catalyst is selected from the group consisting of Ni, Co and Fe.

22. The process according to claim 21 wherein said metal deposited into said nanotubes by electroless deposition includes a metal selected from the group consisting of Ni, Co, Fe, Ag and their alloys.

23. The process according to claim 21 wherein said metal deposited into said nanotubes by electroless deposition includes a metal selected from the group consisting of Ag, Cu, Bi, Pb and Sn.

* * * * *

US006346189B1

(12) **United States Patent**   (10) **Patent No.:**   **US 6,346,189 B1**
Dai et al.   (45) **Date of Patent:**   ***Feb. 12, 2002**

(54) **CARBON NANOTUBE STRUCTURES MADE USING CATALYST ISLANDS**

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(*) Notice: This patent issued on a continued prosecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. 154(a)(2).

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/133,948**

(22) Filed: **Aug. 14, 1998**

(51) Int. Cl.[7] **G01B 5/28**
(52) U.S. Cl. .... **205/766; 423/445 R; 423/453; 73/105**
(58) Field of Search .... 205/766; 423/445 R, 423/453; 73/105

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(57)   **ABSTRACT**

The present invention includes several nanotube structures which can be made using catalyst islands disposed on a substrate (e.g. silicon, alumina, or quartz) or on the free end of an atomic force microscope cantilever. The catalyst islands are capable of catalyzing the growth of carbon nanotubes from carbon containing gases (e.g. methane). The present invention includes an island of catalyst material (such as Fe_2O_3) disposed on the substrate with a carbon nanotube extending from the island. Also included in the present invention is a pair of islands with a nanotube extending between the islands, electrically connecting them. Conductive metal lines connected to the islands (which may be a few microns on a side) allows for external circuitry to connect to the nanotube. Such a structure can be used in many different electronic and microelectromechanical devices. For example, a nanotube connected between two islands can function as a resonator if the substrate beneath the nanotube is etched away. Also, the present invention includes a catalyst particle disposed on the free end of an AFM cantilever and having a nanotube extending from the particle. The nanotube can be used as the scanning tip of the AFM as is know in the art.
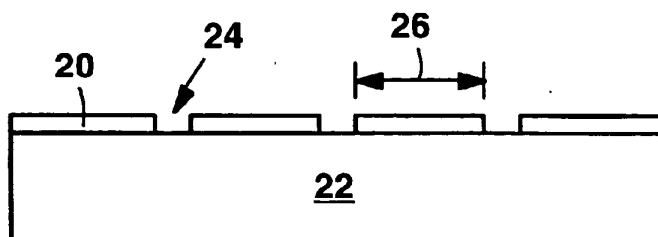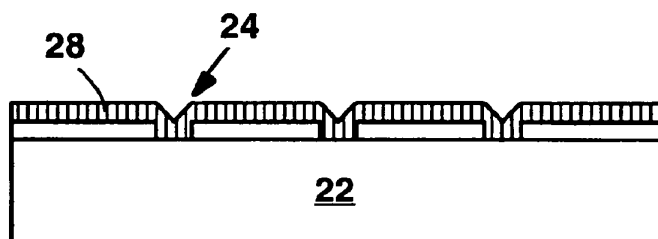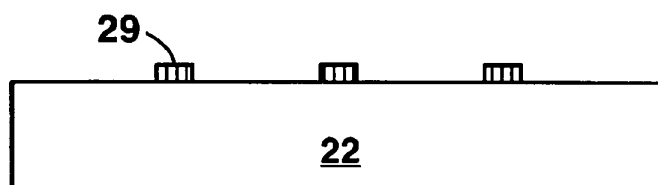
45 Claims, 6 Drawing Sheets
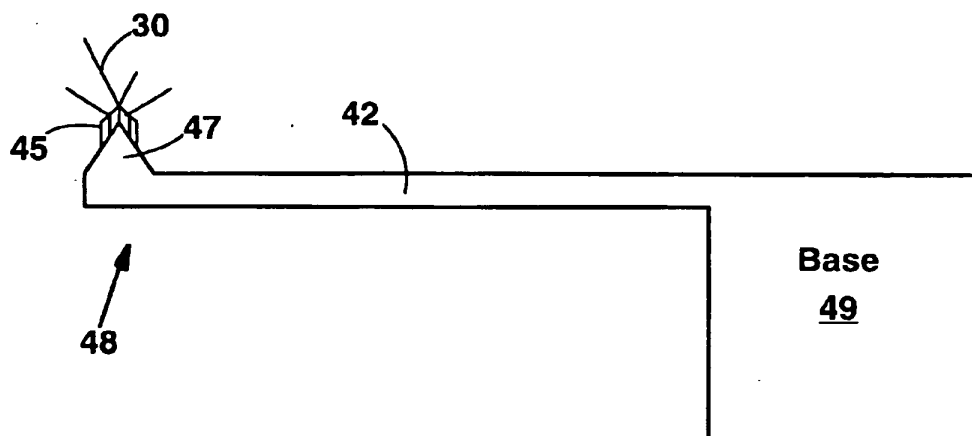
Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

34   37   30a   37   34

29   Substrate **22**   29

Fig. 8A

60   30a

29   Substrate **22**   29

Fig. 8B

61   30a   61   60

29   Substrate **22**   29

Fig. 8C

34   30a   34

29   Substrate **22**   29

Fig. 9

Fig. 10

35

22

Fig. 11A

29   **36**   **30b**   **35**   **29**

22

Fig. 11B

30

45   **47**   **42**

48

Fig. 12

Base
49
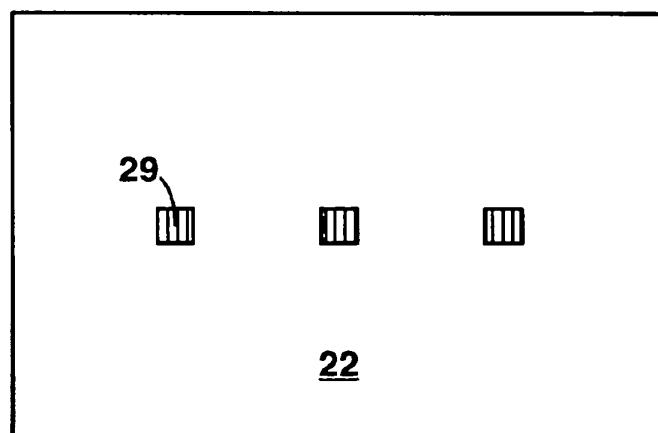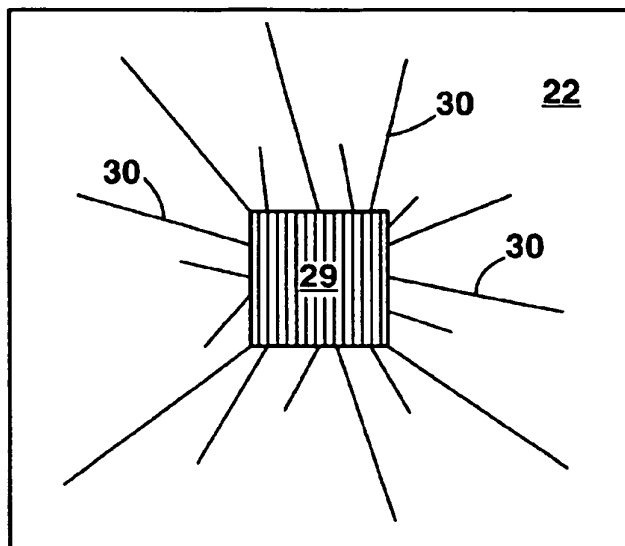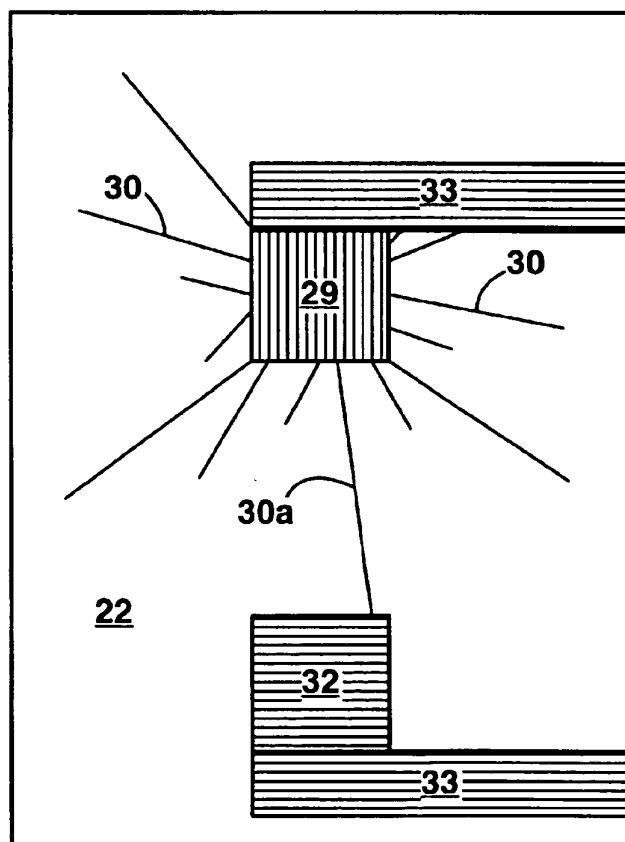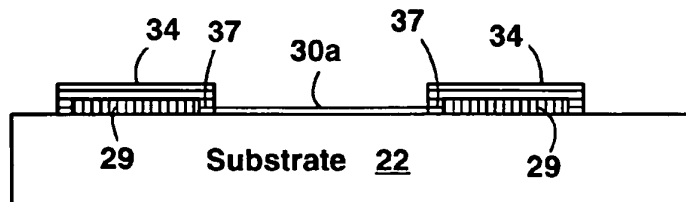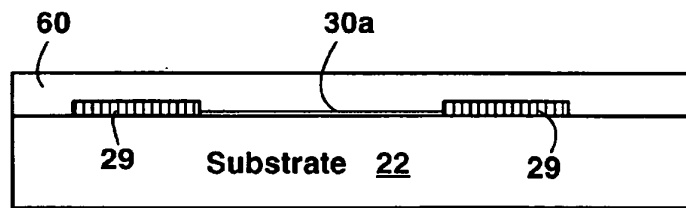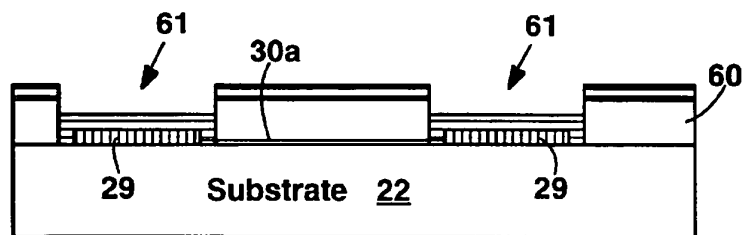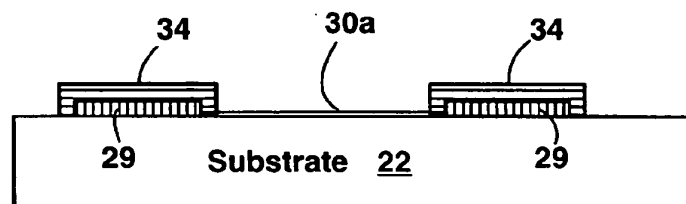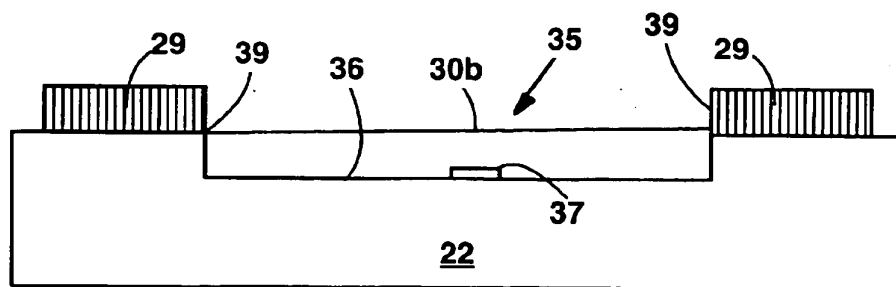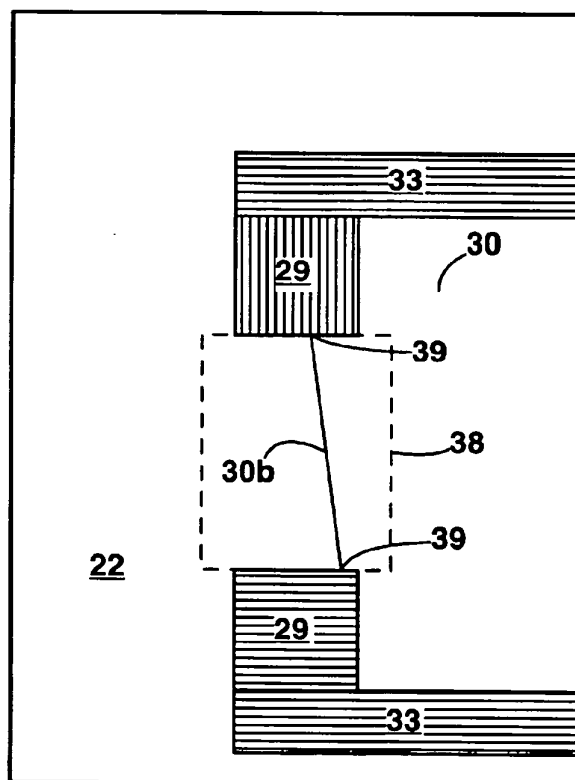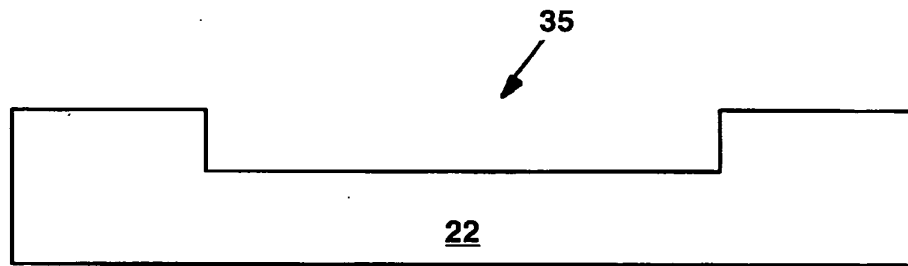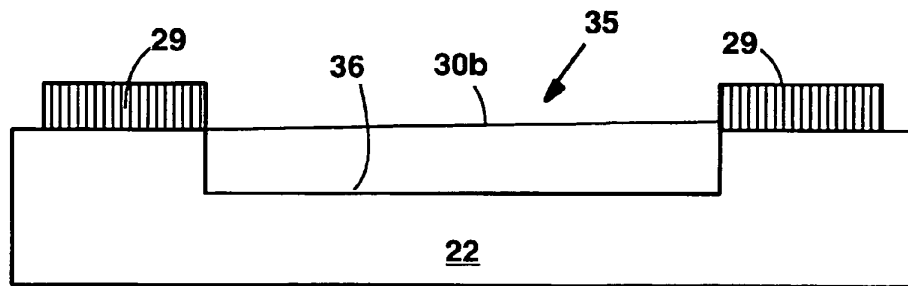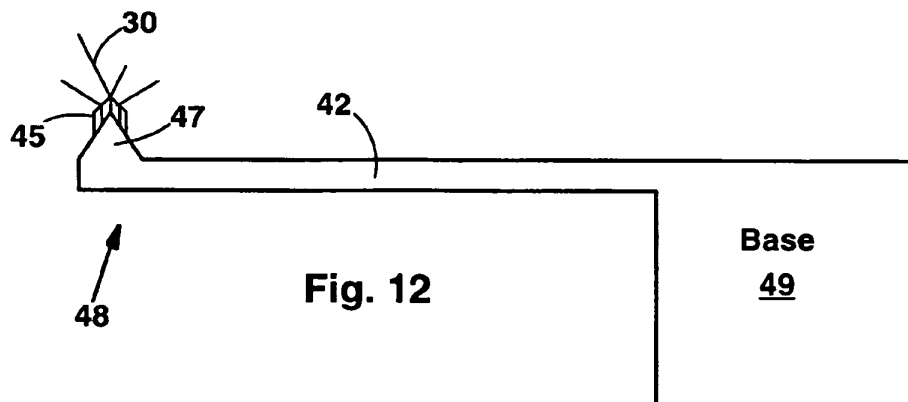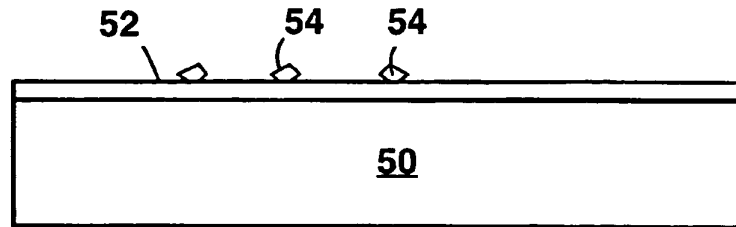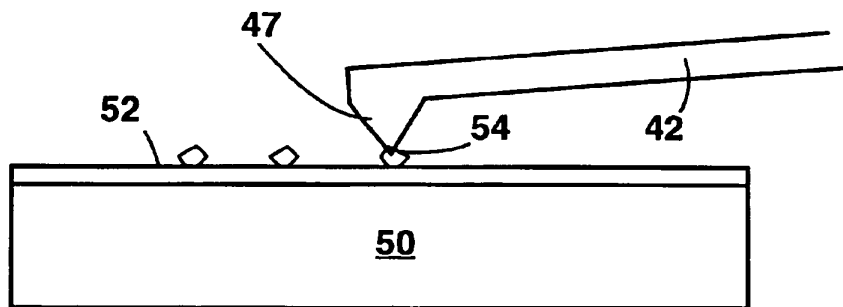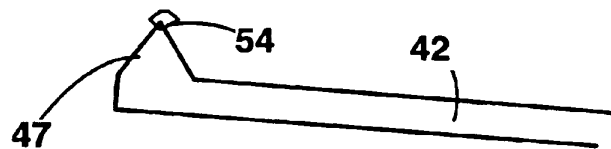
Fig. 13A
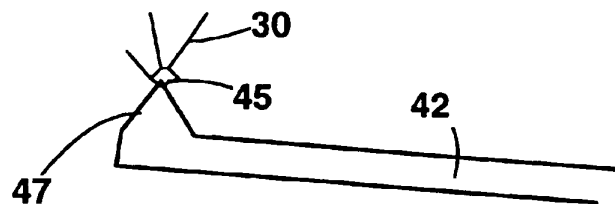
Fig. 13B

Fig. 13C

Fig. 13D

CARBON NANOTUBE STRUCTURES MADE USING CATALYST ISLANDS

FIELD OF THE INVENTION

The present invention relates generally to the fabrication of nanotubes, and in particular to methods of fabricating nanotube structures from an array of catalyst islands on a semiconductor surface.

BACKGROUND OF THE INVENTION

Carbon nanotubes are recently discovered, hollow graphite tubules. When isolated, individual nanotubes are useful for making microscopic electrical, mechanical, or electro-mechanical devices. Obtaining individual, high quality, single-walled nanotubes has proven to be a difficult task, however. Existing methods for the production of nanotubes, including arc-discharge and laser ablation techniques, yield bulk materials with tangled nanotubes. The nanotubes in the bulk materials are mostly in bundled forms. These tangled nanotubes are extremely difficult to purify, isolate, manipulate, and use as discrete elements for making functional devices.

One conventional method for producing carbon nano-tubes is disclosed in U.S. Pat. No. 5,482,601 issued to Oshima et al. on Jan. 9, 1996. The nanotubes are produced by successively repositioning a rod-like, carbon anode relative to a cathode surface such that a tip of the anode successively faces different portions of the cathode surface. A direct current voltage is impressed between the tip of the anode and the cathode surface so that an arc discharge occurs with the simultaneous formation of carbonaceous deposits containing carbon nanotubes on the cathode surface. The carbonaceous deposits are scraped and collected.

U.S. Pat. No. 5,500,200 issued to Mandeville et al. on Mar. 19, 1996 discloses a method for the bulk production of multi-walled tubes. According to the method, a catalyst is prepared using particles of fumed alumina with an average particle size of about 100 Å. Iron acetylacetonate is deposited on the alumina particles, and the resultant catalyst particles are heated in a hydrogen/ethylene atmosphere. The catalyst particles are preferably reacted with the hydrogen/ethylene mixture for about 0.5 hours in a reactor tube, after which the reactor tube is allowed to cool to room temperature under a flow of argon. Harvesting of the carbon tubes so produced showed a yield greater than 30 times the weight of the iron in the catalyst particles.

Although the methods described by Oshima and Mandeville are effective for producing bulk amounts of carbon tubes or carbon fibrils, the resulting bulk materials are "hairballs" containing tangled and kinked tubes which one collects into vials or containers. These bulk materials are useful to put into polymers or metals to make composites that exhibit improved properties of the polymers or metals. For making functional microscopic devices, however, these bulk materials are nearly useless because it is nearly impossible to isolate one individual tube from the tangled material, manipulate the tube, and construct a functional device using that one tube. Also, many of the tubes have molecular-level structural defects which results in weaker tubes with poor electrical characteristics.

Atomic force microscopes (AFMs) sometimes employ nanotubes as the scanning tip because nanotubes are resilient and have an atomically sharp tip. However, the manufacturing of nanotube-tipped AFM devices is problematic because the nanotubes must be painstakingly separated from disorganized bundles of nanotubes and attached to the AFM

cantilever. It would be an advance in the art of atomic force microscopy to provide a nanotube-tipped AFM device that is simpler to manufacture.

OBJECTS AND ADVANTAGES OF THE INVENTION

In view of the above, it is an object of the present invention to provide a method for the large scale synthesis of individual distinct single-walled nanotubes. In particular, it is an object of the present invention to provide such a method which allows nanotube growth to be confined to desired locations so that the nanotubes can be easily addressed and integrated into structures to obtain functional microscopic devices. It is a further object of the invention to provide a method for integrating the nanotubes into semi-conductor microstructures to obtain a variety of nanotube devices. Further, it is an object of the present invention to provide a nanotube-tipped atomic force microscope device which is simple to manufacture.

These and other objects and advantages will become more apparent after consideration of the ensuing description and the accompanying drawings.

SUMMARY

These objects and advantages are provided by an apparatus including a substrate and a catalyst island disposed on the substrate. The catalyst island includes a catalyst particle that is capable of growing carbon nanotubes when exposed to a hydrocarbon gas at elevated temperatures. A carbon nanotube extends from the catalyst particle. The nanotube may be in contact with a top surface of the substrate.

The substrate may be made of silicon, alumina, quartz, silicon oxide or silicon nitride. The nanotube may be a single-walled nanotube. The catalyst may include Fe_2O_3 or other catalyst materials including molybdenum, cobalt, nickel, or zinc and oxides thereof (iron molybdenum, and ruthenium oxides are preferred). The catalyst island is preferably about 1–5 microns in size.

The present invention also includes an apparatus having a substrate with two catalyst islands and a nanotube extending between the islands. The nanotube provides an electrical connection between the islands, which are electrically conductive. Conductive lines can provide electrical connections to the islands and nanotube. The nanotube may be freestanding above the substrate. A freestanding nanotube can be used as a high frequency, high-Q resonator.

Alternatively, one of the islands is replaced with a metal pad that does not have catalytic properties.

The present invention also includes an atomic force microscopy apparatus that has a catalyst particle disposed on a free end of a cantilever. A nanotube extends from the catalyst particle. The nanotube can be used as the scanning tip of the atomic force microscope apparatus.

The present invention also includes a method of making individually distinct nanotubes on a substrate surface. The method begins with disposing catalyst islands on the surface of a substrate. Then, the catalyst islands are contacted with methane gas at elevated temperature. The nanotubes grown are separate and extend over the surface of the substrate. The separate and distinct nanotubes can be incorporated into microelectronic or microelectromechanical devices.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a first step in making nanotubes according to the present invention.

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FIG. 2 shows a second step in making nanotubes according to the present invention.

FIG. 3 shows a third step in making nanotubes according to the present invention.

FIG. 4 shows a top view of a substrate with three catalyst islands.

FIG. 5 shows a closeup top view of a single catalyst island which has been used to grow nanotubes.

FIG. 6 shows an apparatus according to the present invention which has a nanotube connected between a catalyst island and a metal pad.

FIG. 7 shows a preferred embodiment of the present invention in which metal covers are disposed on top of the catalyst islands and portions of the nanotubes.

FIG. 8A–8C illustrate how the metal covers of FIG. 7 can be made.

FIG. 9 shows a side view of a resonator according to the present invention made from a freestanding nanotube supported by the ends of the nanotube.

FIG. 10 shows a top view illustrating how the apparatus of FIG. 9 can be made.

FIGS. 11A and 11B illustrate an alternative method of making the apparatus of FIG. 9.

FIG. 12 shows an atomic force microscope tip made according to the present invention.

FIGS. 13A–13D illustrate a method of producing a carbon nanotube on a tip of an atomic force microscope cantilever according to the present invention.

DETAILED DESCRIPTION

FIG. 1 shows a first step in a method of the present invention for making individual carbon nanotubes which are individually separable and distinct. A layer of resist 20 is disposed and patterned on a top surface of a substrate 22. Patterning can be performed by e-beam lithography. The substrate 22 can be made of silicon, alumina, quartz, silicon oxide or silicon nitride for example. The substrate can also have a metal film on top.

The patterned resist 20 has holes 24 which expose the underlying substrate 22. The holes 24 are about 3–5 microns in size and spaced apart by a distance 26 of about 10 microns. The resist may have a single hole or many holes 24.

Next, in FIG. 2, a solution of $Fe(NO_3)_3$ in methanol, mixed with alumina nanoparticles (about 15–30 nanometers in size, for example) is deposited on the surfaces of the resist 20 and substrate 22. In a specific example, catalyst preparation includes mixing 4.0 grams of alumina nanoparticles with 1.0 gram of $Fe(NO_3)_3*9H_2O$ in 30 mL methanol for 24 hours. After applying the mixture to the substrate, the solvent (i.e. methanol) is evaporated, leaving alumina nanoparticles coated with metal salt (i.e. $Fe(NO_3)_3$) 28 adhering to the resist and in the holes 24. Next, in FIG. 3, a lift-off process is performed, leaving isolated (nonconnected) islands 29 of $Fe(NO_3)_3$-coated nanoparticles adhering in regions where holes 24 existed. FIG. 4 shows a top view of the islands 29.

Heating the substrate 22 and nanoparticles decomposes the $Fe(NO_3)_3$ to Fe_2O_3. This is performed by placing the substrate in a furnace with an Argon atmosphere and heating to about 100–400° Celsius. The Fe_2O_3/nanoparticle mixture is an active catalyst which will catalyze the formation of carbon nanotubes when exposed to methane gas at elevated temperature.

Growth of single-walled nanotubes is performed by heating the substrate with catalyst islands in the furnace at about

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850–1000° C. and flowing 99.99% pure methane over the catalyst islands 29 at a velocity of about 2–20 centimeters per second (e.g., for a 1-inch diameter tube, flowing methane at a rate of about 600–6000 cm^3/min). Use of these parameters results in nanotubes which are substantially perfect and straight, with no structural flaws (i.e. all the carbon rings in the nanotubes have 6 carbon atoms instead of 5 or 7 carbon atoms). Most of the nanotubes are single-walled, with diameters in the range of about 1–5 nanometers. When grown at 1000° C., 90% of the tubes were single-walled; when grown at 900° C., 99% of the tubes were single-walled. Most of the nanotubes have diameters in the range of 1–2 nanometers. The nanotubes have large aspect ratios (length/diameter) approaching about 10,000, and are very straight (a result of the absence of structural flaws).

It is noted that many different recipes for nanotube catalysts are known in the art. For example, $Fe(SO_4)$ or other Iron salts can be substituted for the $Fe(NO_3)_3$. The quality of the nanotubes depends upon the catalyst material used. Iron, molybdenum and zinc oxides are preferred for making high quality tubes. A particularly good catalyst is made with a mixture of iron, molybdenum and ruthenium oxides. Most generally, both elemental metals and their oxides can be used to grow nanotubes.

Also, the nanoparticles can be made of many ceramic materials besides alumina. Silica, for example, can also be used. Generally, refractory oxide ceramic materials can be used in place of the alumina nanoparticles. Still further, nanoparticles may not be used at all. Small quantities of Iron salts can be deposited on the substrate (for example, by dissolving in a solvent and evaporating the solvent) and heated to decomposition without being mixed with nanoparticles.

FIG. 5 shows a closeup top view of the island 29 and substrate after the growth of nanotubes has been performed. Carbon nanotubes 30 extend from the island 29 in random directions. The carbon nanotubes 30 are not freestanding, but are disposed in contact with the substrate surface. Also, the carbon nanotubes are firmly attached to the island 29. The nanotubes generally grow in a 'base-growth' mode, where new carbon is added to the nanotubes 30 at the point where they are attached to the island 29. The nanotubes are attached at one end to the island, and the opposite end is free. The nanotubes can be used as resonators by allowing the free end to vibrate.

The carbon nanotubes 30 are not tangled together, but are individually separable. This is due to the fact that a small number of nanotubes grow from each island. Also, the nanotubes are spaced apart by a substantial distance. Typically, about 10–50 nanotubes are grown from each island. If larger numbers of nanotubes are grown (e.g. by using a more effective catalyst), then the nanotubes may form bundles. This is undesirable for applications requiring single distinct nanotubes. However, bundles of nanotubes can also be useful for many electrical and mechanical devices such as interconnects, field effect transistors, single electron transistors, and resonators which have only one fixed end.

Individually separable nanotubes are useful for the manufacturing of electronic and micromechanical devices because individual nanotubes can be incorporated into the devices by appropriately locating islands 29. Electrical and mechanical connections can be made to individual nanotubes if they are spatially separated and distinct.

FIG. 6 shows a top view of an electronic device made by locating the island 29 close to a patterned metal pad 32. A

single nanotube 30a extends from the island 29 to the metal pad 32, thereby providing electrical contact between the island 29 and pad 32. The island 29 and pad 32 are spaced apart by a distance in the range of 100 nanometers to about 5 microns. The island 29 and pad 32 are both electrically conductive, so patterned conductive lines 33 on the substrate surface can provide for macroscopic electrical connections to the nanotube 30a. The nanotube 30a with a macroscopic electrical connection on each end can be used in many devices including field-effect transistors, single electron transistors, or low current value fuses.

The conductive lines 33 may be applied to the substrate 20 before the islands 29 are deposited. In this way, the islands rest on top of the conductive lines 33. Also, the conductive lines 33 can be disposed on top of the islands (by applying the conductive lines on top of the islands. The conductive lines can be deposited before or after the growth of nanotubes.

The apparatus of FIG. 6 is made by simply locating the island and metal pad proximate to one another and catalytically growing nanotubes from the island. The closer the island 29 and pad 32, the more likely that a nanotube will be grown that connects the island and pad.

Also, two or more nanotubes can simultaneously electrically connect the island 29 and metal pad 32. If multiple nanotubes connect between the island and pad, then all but one of the nanotubes can be broken with an AFM tip. This is performed by dragging the AFM tip across the substrate surface so that it bends unwanted nanotubes until they break.

Further, a second catalyst island can be substituted for the metal pad 32. In such a device, the nanotube 30a provides electrical contact between two catalyst islands 29 instead of between an island 29 and a metal pad 32. Metal lines 33 can provide electrical connections to each catalyst island as in FIG. 6. The same spacing distance can be used (100 nanometers to about 5 microns) if a catalyst island is substituted for the metal pad.

FIG. 7 shows a side view of a preferred embodiment of the present invention in which a metal cover 34 is deposited on top of each catalyst island 29. The metal covers 34 can be made of platinum or titanium-gold alloy, for example. Each metal cover 34 covers a portion of each island 29 and covers an end portion 37 of the nanotube 30a. The metal cover therefore serves to help hold the nanotube 30a rigidly in place.

The metal covers 34 help to provide Ohmic electrical connections to the ends of the nanotube 30a. Ohmic electrical connections with the nanotube are assured by heating the apparatus after depositing the metal covers 34. For example, heating the apparatus to about 300° C. in air will result in Ohmic electrical connections between the metal covers 34 and nanotube 30a. Metal lines 33 as shown in FIG. 6 can be connected to the metal covers to provide macroscopic electrical connections with the nanotube 30a. Electrical conduction through the catalyst island is therefore not necessary.

The metal covers 34 can be made by lithographically patterning the metal comprising the covers 34. FIGS. 8A–8C illustrate how this can be done. First, a layer of spin-on resist 60 is deposited on top of the islands 29 and nanotube 30a. Next, the resist 60 is etched in regions 61 where the metal cover 34 is to be located. The metal comprising the metal covers 34 is then deposited (by physical vapor deposition or CVD processes, for example), and the resist 60 is removed in a lift-off process which leaves only the metal covers 34.

The present invention can provide freestanding nanotubes capable of acting as high-Q resonators. FIG. 9 shows a side

view of a device including a freestanding nanotube 30b. The freestanding nanotube 30b is suspended above the substrate 22 which is depressed in a trench region 35 between the islands 29. The trench 35 can be formed by etching the substrate. The nanotube 30b therefore lies above a surface 36 of the etched substrate 22 and is supported only by nanotube ends 39. The trench 35 and metal covers 34 can be combined in the same apparatus.

The nanotube 30b can be resonated by locating the nanotube 30b in a magnetic field (perpendicular to the length of the nanotube 30b) and passing an oscillating current through the nanotube. A conductive film 37 capacitively coupled with the nanotube 30b extracts a resonant signal from the nanotube. Alternatively, the conductive film 37 can be used to electrostatically excite mechanical vibrations in the nanotube 30b.

FIG. 10 shows a top view of the substrate 22 and islands 29 illustrating how the apparatus of FIG. 9 can be made. First, the nanotube 30b which connects the islands 29 is grown. Other nanotubes will also be grown from both islands, but they are not shown for clarity. Then, all regions of the substrate except for a region defined by a box 38 are masked with resist. Spin-on resist can be used, for example. The act of spin-coating resist on the substrate will not damage the nanotube 30b. Next, the region inside the box 38 is exposed to an etchant which removes substrate material, but does not affect the nanotube 30b. Many different etchants can be used, depending upon the composition of the substrate (e.g. hydrofluoric acid can be used to etch SiO_2 or Si substrates). Etching the substrate 22 under the nanotube 30b results in the nanotube being supported only at its ends 39. Metal lines 33 provide macroscopic electrical connections to the nanotube 30b through the catalyst islands 29. Also, metal covers 34 can be deposited before or after etching the trench 35 to provide Ohmic electrical connections to the nanotube and improved mechanical stability for the nanotube ends 39.

An alternative method for making the apparatus of FIG. 9 is shown in the side views of FIGS. 11A and 11B. In FIG. 11A, the substrate 22 is etched to form the trench 35 where the nanotube 30b is suspended. Then islands 29 are disposed on opposite sides of the trench 35 and nanotubes are grown from the islands 29. The nanotube 30b that connects the islands grows from one island to the other. Alternatively, one of the islands can be replaced with the metal pad 32, in which case the nanotube grows from the island 29 to the pad 32. Also, metal covers 34 can be deposited on top of the nanotube 30b and catalyst islands 29.

The present invention includes an embodiment where the freestanding nanotube is only supported on one end by a catalyst island 29 (i.e. the freestanding nanotube does not extend all the way across the trench 35). The nanotube is therefore a cantilever, and can be used as a resonator.

It is noted that growing nanotubes between islands, or between an island and a metal pad is an uncertain endeavor. One cannot be sure that a particular arrangement of catalyst islands will result in a nanotube connection between a particular pair of islands, or how many nanotubes will connect. However, if a pair of islands are spaced less than about 10 microns apart, and are at least 1 micron wide, a nanotube is likely to connect the pair of islands. At least one bridging nanotube connection can be practically assured if a number of islands are disposed with various spacings in an array.

FIG. 12 shows another embodiment of the present invention in which a catalyst particle 45 is located on a tip 47 of

an atomic force microscope (AFM) cantilever 42. The cantilever 42 is supported by a base 49, and has a free end 48 opposite the base 49. The particle 45 may be made of Fe_2O_3 (decomposed from $Fe(NO_3)_3$), for example. The catalyst particle 45 may or may not have supporting nanoparticles (i.e. silica or alumina particles). The catalyst particle is firmly attached to the tip 47. Nanotubes 30 grown from the particle 45 are firmly attached to the cantilever and are atomically sharp. Nanotubes grown from the catalyst particle can be used as probe tips for AFM. Alternatively, the cantilever does not have a tip 47, and the particle is disposed directly on the cantilever 42.

FIGS. 13A and 13B illustrate how the apparatus of FIG. 12 can be made. First, in FIG. 13A, a substrate 50 is coated with a gold film 52, and then droplets of $Fe(NO_3)_3$ dissolved in methanol are deposited on the gold surface. The methanol is then evaporated leaving only small particles 54 of $Fe(NO_3)_3$ on the gold film 52. Next , as shown in FIG. 13B, the AFM tip 47 is brought into contact with a particle 54 of $Fe(NO_3)_3$. An electric field is then applied between the tip 47 and the gold film 52. The electric field causes the $Fe(NO_3)_3$ particle to adhere to the tip 47 and may cause the $Fe(NO_3)_3$ to decompose into Fe_2O_3. Then, in FIG. 13C, the cantilever 42 and tip 47 with the adhered $Fe(NO_3)_3$ particle 54 is removed from the gold film 52. In FIG. 13D, the device is heated to fully decompose the $Fe(NO_3)_3$ particle 54. into Fe_2O_3. This transforms the $Fe(NO_3)_3$ particle 54 into a catalyst particle 45 (shown in FIG. 12). Then, nanotubes 30 are grown from the catalyst particle 45.

An AFM cantilever with a catalytically grown nanotube tip has several advantages over an AFM cantilever with a nanotube bonded with other techniques. It is a relatively simple task to catalytically grow a nanotube from the catalyst particle on the cantilever. Also, the nanotube is firmly bonded to the cantilever.

It will be clear to one skilled in the art that the above embodiment may be altered in many ways without departing from the scope of the invention. Accordingly, the scope of the invention should be determined by the following claims and their legal equivalents.

What is claimed is:

1. An apparatus comprising:
   a) a substrate with a top surface;
   b) a catalyst island disposed on the top surface of the substrate;
   c) a carbon nanotube extending from the catalyst island.

2. The apparatus of claim 1 wherein the nanotube is disposed on the top surface of the substrate.

3. The apparatus of claim 1 wherein the nanotube is a single-walled nanotube.

4. The apparatus of claim 1 wherein the catalyst island comprises Fe_2O_3.

5. The apparatus of claim 1 wherein the catalyst island comprises a material selected from the group consisting of iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof.

6. The apparatus of claim 5 wherein the catalyst island comprises a material selected from the group consisting of iron, molybdenum, ruthenium and oxides thereof.

7. The apparatus of claim 1 wherein the catalyst island is in the range of 1–5 microns in size.

8. The apparatus of claim 1, wherein the substrate comprises a material selected from the group consisting of silicon, alumina, quartz, and silicon nitride.

9. The apparatus of claim 1 wherein the catalyst island comprises particles of ceramic material.

10. The apparatus of claim 1 further comprising a metal cover which covers an end portion of the nanotube and a portion of the island.

11. An apparatus comprising:
   a) a substrate with a top surface;
   b) two catalyst islands disposed on the top surface of the substrate;
   c) a carbon nanotube extending between the catalyst islands such that the nanotube provides an electrical connection between the catalyst islands.

12. The apparatus of claim 11 wherein the nanotube is disposed on the top surface of the substrate.

13. The apparatus of claim 11 wherein the nanotube is supported only by its ends.

14. The apparatus of claim 11 wherein the substrate comprises a trench under the nanotube so that the nanotube is freestanding.

15. The apparatus of claim 11 wherein the catalyst island comprises particles of ceramic material.

16. The apparatus of claim 11 further comprising a conductive line in electrical contact with each island.

17. The apparatus of claim 11 wherein the catalyst islands are separated by a distance less than about 50 microns.

18. The apparatus of claim 11, wherein the substrate comprises a material selected from the group consisting of silicon, alumina, quartz, silica and silicon nitride.

19. The apparatus of claim 11 wherein the catalyst islands comprise a material selected from the group consisting of iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof.

20. The apparatus of claim 19 wherein the catalyst islands comprise a material selected from the group consisting of iron, molybdenum, ruthenium and oxides thereof.

21. The apparatus of claim 11 further comprising a metal cover which covers an end portion of the nanotube and a portion of at least one island.

22. An apparatus comprising:
   a) a substrate with a top surface;
   b) a catalyst island disposed on the top surface of the substrate;
   c) a metal pad disposed on the top surface of the substrate;
   d) a carbon nanotube extending between the catalyst island and the metal pad such that the nanotube provides an electrical connection between the catalyst island and metal pad.

23. The apparatus of claim 22 wherein the nanotube is disposed on the top surface of the substrate.

24. The apparatus of claim 22 wherein the nanotube is supported only by its ends.

25. The apparatus of claim 22 wherein the substrate comprises a trench under the nanotube so that the nanotube is freestanding.

26. The apparatus of claim 22 wherein the catalyst island comprises particles of ceramic material.

27. The apparatus of claim 22 further comprising a conductive line in electrical contact with the island.

28. The apparatus of claim 22 further comprising a conductive line in electrical contact with the metal pad.

29. The apparatus of claim 22, wherein the substrate comprises a material selected from the group consisting of silicon, alumina, quartz, silica and silicon nitride.

30. The apparatus of claim 22 wherein the catalyst island comprises a material selected from the group consisting of iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof.

31. The apparatus of claim 30 wherein the catalyst island comprises a material selected from the group consisting of iron, molybdenum, ruthenium, and oxides thereof.

32. The apparatus of claim 22 further comprising a metal cover which covers an end portion of the nanotube and a portion of the island.

33. An apparatus comprising:

a) a base;

b) a cantilever extending from the base, the cantilever having a free end opposite the base;

c) a catalyst particle disposed on the free end of the cantilever, wherein the catalyst particle is capable of catalyzing the growth of carbon nanotubes;

d) a carbon nanotube extending from the catalyst particle.

34. The apparatus of claim 33 wherein the catalyst particle comprises Fe_2O_3.

35. The apparatus of claim 33 wherein the catalyst particle comprises a material selected from the group consisting of iron, molybdenum, cobalt, nickel, ruthenium, zinc and oxides thereof.

36. The apparatus of claim 33 further comprising a tip on the free end, wherein the catalyst particle is disposed on the tip.

37. The apparatus of claim 33 wherein the apparatus is an atomic force microscopy apparatus.

38. A method for producing an apparatus with a tip comprising a carbon nanotube, the method comprising the steps of:

a) providing a cantilever suitable for use in atomic force microscopy;

b) disposing a catalyst particle on a free end of the cantilever, wherein the catalyst particle is capable of growing carbon nanotubes when exposed to a carbon-containing gas at elevated temperature;

c) contacting a carbon-containing gas to the catalyst particle at elevated temperature.

39. The method of claim 38 wherein step (b) comprises the steps of:

i) contacting the free end to a particle of $Fe(NO_3)_3$ disposed on an electrically conductive substrate; and

ii) applying an electric field between the free end and the substrate.

40. The method of claim 38 wherein step (b) comprises the steps of:

i) contacting the free end to a particle of $Fe(SO_4)_2$ disposed on an electrically conductive substrate; and

ii) applying an electric field between the free end and the substrate.

41. The method of claim 38 wherein the apparatus produced is an atomic force microscopy apparatus.

42. A method for producing individually distinct carbon nanotubes, the method comprising the steps of:

a) providing a substrate with a top surface;

b) forming an island of catalyst material on the top surface;

c) heating the substrate and catalyst island; and

d) contacting the catalyst island with a carbon-containing gas for a period of time sufficient to form the nanotubes on the catalyst island.

43. The method of claim 42 wherein the catalyst island is about 1–5 microns in size.

44. The method of claim 42, wherein the carbon-containing gas comprises methane.

45. The method of claim 42, wherein the period of time is about 10 minutes.

* * * * *

(12) **United States Patent**

Hsu

(10) **Patent No.:** **US 6,448,701 B1**

(45) **Date of Patent:** **Sep. 10, 2002**

(54) **SELF-ALIGNED INTEGRALLY GATED NANOFILAMENT FIELD EMITTER CELL AND ARRAY**

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(73) Assignee: **The United States of America as represented by the Secretary of the Navy**, Washington, DC (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/804,641

(22) Filed: **Mar. 9, 2001**

(51) Int. Cl.^{7} H01J 1/30

(52) U.S. Cl. 313/309; 313/336; 313/351; 313/497; 313/311

(58) Field of Search 313/309, 336, 313/351, 495, 497, 311

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(57) **ABSTRACT**

The present invention discloses a new field emitter cell and array consisting of groups of nanofilaments forming emitter cathodes. Control gates are microprocessed to be integrally formed with groups of nanofilament emitter cathodes on a substrate. Groups of nanofilaments are grown directly on the substrate material. As a result, the control gates and groups of nanofilaments are self-aligned with one another.
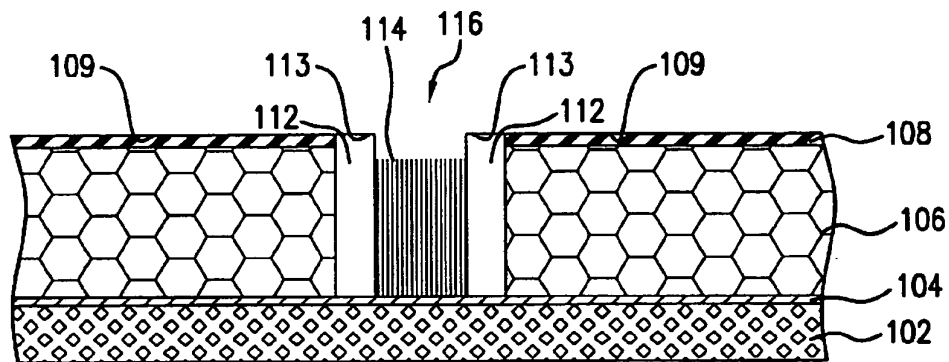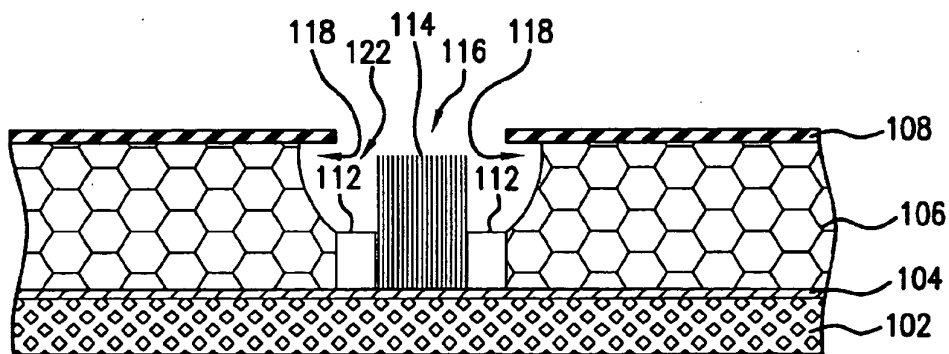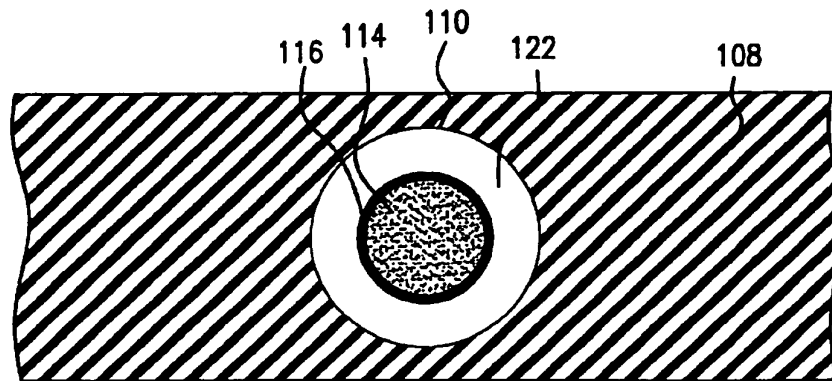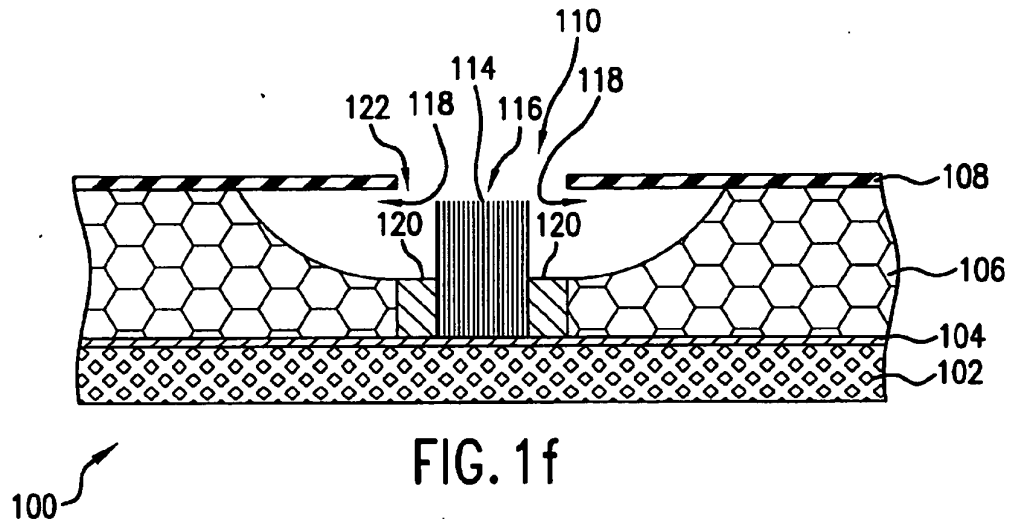
28 Claims, 19 Drawing Sheets

110

108
106
104
102

FIG. 1a

100

110 112

109 109

108
106
104
102

FIG. 1b

100

110

109 112 112 109

108
106
104
102

FIG. 1c

100

FIG. 1d

FIG. 1e

FIG. 1f

FIG. 1g

210

208

206

203

202

FIG. 2a

200

210

212

208

206

202

FIG. 2b

200

209   210   209
212   208

203   206

202

FIG. 2c

200

209 212 210 209 224
204
208
206
202
203

FIG. 2d

200

212 210
208
224 206
202
204

FIG. 2e

200

214 212
208
206
202
204

FIG. 2f

200

218   214   210   216   212   208   206   202

FIG. 2g

200

304
330
302
300

FIG. 3a

314
316
304
330
302
300

FIG. 3b

316
314
312
304
302
300

FIG. 3c

316

314

332

312

302

300

FIG. 3d

316

334

332

312

302

300

FIG. 3e

FIG. 3f

FIG. 3g

FIG. 4a

FIG. 4b

FIG. 4c

430

418   418

408

432

412

402

400

FIG. 4d

440   440   440

418   418

408

408

432

412

400

FIG. 4e

430

440   440   408

432

412

400

FIG. 4f

FIG. 4g

FIG. 4h

FIG. 4i

510

508

530

532

502

500

FIG. 5a

504   511   504

518   508

531   518   532

502

501

FIG. 5b

FIG.5c

FIG.5d

FIG.5e

FIG. 6a

FIG. 6b

FIG. 7a

FIG. 7b

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SELF-ALIGNED INTEGRALLY GATED NANOFILAMENT FIELD EMITTER CELL AND ARRAY

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a field emitter cell and array, in particular, to an integrally gated, self-aligned field emitter cell and array whose cathode is formed of a recently discovered class of materials of nanotubes and nanowires, collectively referred to as nanofilaments.

BACKGROUND OF THE INVENTION

Field emitters arrays (FEAs) are naturally small structures which provide reasonably high current densities at low voltages. Typically, FEAs are composed of emitter cells in the form of conical, pyramidal, or cusp-shaped point, edge or wedge-shaped vertical structures. These cells are electrically insulated from a positively charged extraction gate and produce an electron beam that travels through an associated opening in the positively charged gate.

The typical field emitter structure includes a sharp point at the tip of the vertical structure (field emitter) and opposite an electrode. In order to generate electrons which are not collected at the extraction electrode, but can be manipulated and collected elsewhere, an aperture is created in the extraction electrode. The aperture is larger (e.g., two orders of magnitude) than the radius of curvature for the field emitter.

Consequently, the extraction electrode is a flat horizontal surface containing an extraction electrode aperture for the field emitter. Such an extraction electrode is referred to as the gate electrode. The field emitter is centered horizontally in the gate aperture and does not touch the gate although the vertical direction of the field emitter is perpendicular to the horizontal plane of the gate. The positive charges on the edge of the extraction electrode aperture surround the field emitter symmetrically so that the electric field produced between the field emitter and the gate causes the electrons to be emitted from the field emitter in a direction such that the electrons are collected on an electrode (anode) that is separate and distinct from the gate. The smaller the aperture, i.e., the closer the gate is to the field emitter, the lower the voltage required to produce field emission of electrons.
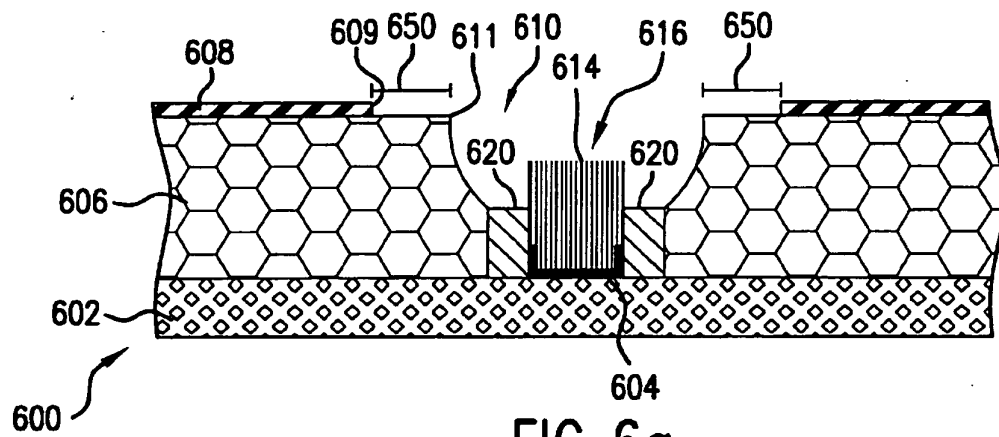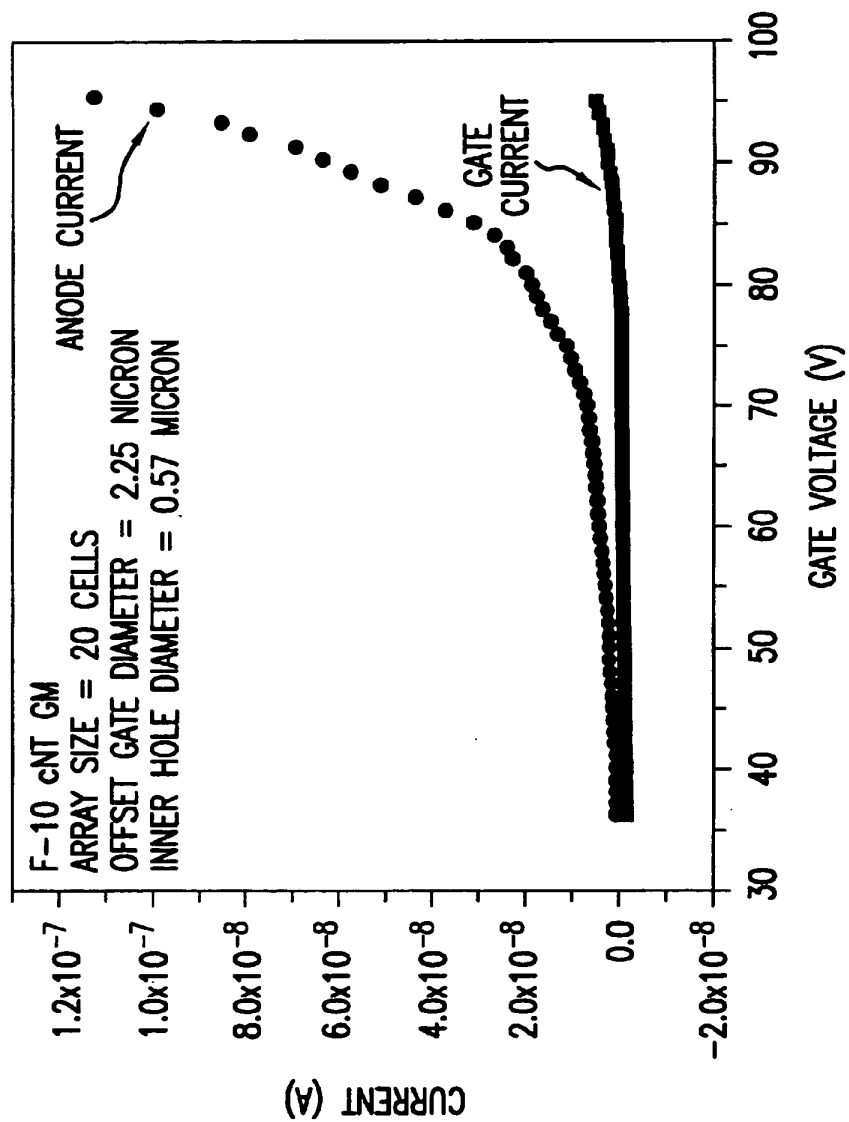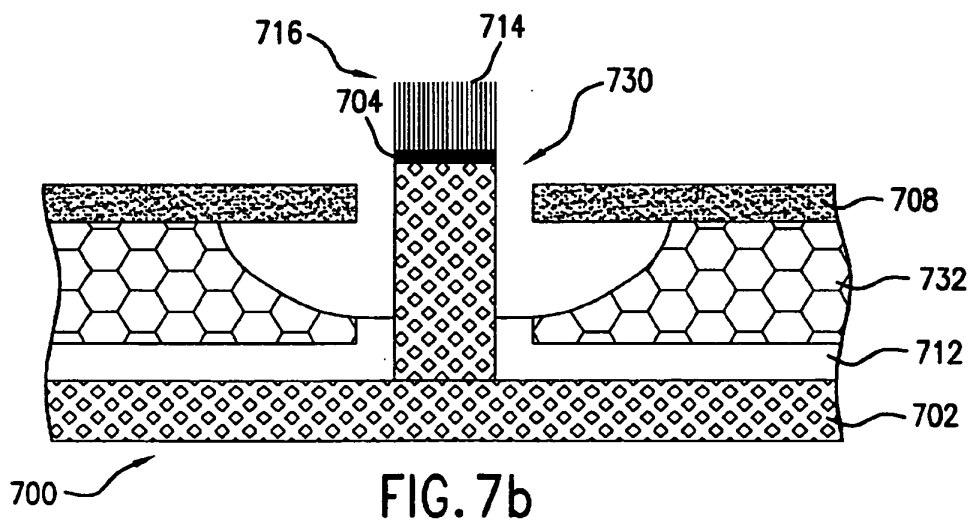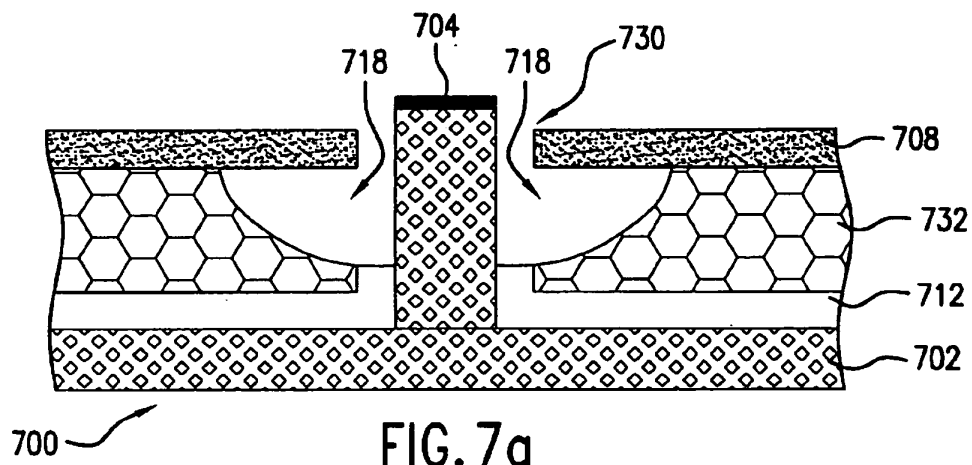
The sharp point at the tip of the field emitter provides for reduction in the voltage necessary to produce field emission of electrons. As a result, numerous micro-manufacturing techniques have been developed to produce various sharp tip designs. Current techniques include wet etching, reactive ion etching (RIE), and a variety of field emitter tip deposition techniques.

Effective methods generally require the use of lithography which has a number of inherent disadvantages including a high equipment and manufacturing cost. For example, the high degree of spatial registration requires expensive high resolution lithography.

Additionally, cathode structures include very small localized vacuum electron sources which emit sufficiently high current. However, these vacuum electron sources are difficult to fabricate for practical applications. This is particularly true when the sources are required to operate at reasonably low voltages. Presently available thermionic sources do not emit high current densities, but rather result in small currents being generated from small areas. In addition, thermionic sources must be heated, and thus

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require special heating circuits and power supplies. Photoemitters have similar problems with regard to low currents and current densities.

Recent advancements in nanotechnology have resulted in the creation of nanofilaments including nanotubes. One such example is carbon nanotubes. These nanotubes behave like metals or semiconductors and can conduct electricity better than copper, transmit heat better than diamond, and are among some of the strongest materials known while being only a few nanometers in diameter. Nanofilaments can have small diameters, ranging down to only a few nanometers. The nanofilaments may be grown to various lengths (e.g., 100–1000 nm) yet their diameter remains uniform. The aspect ratio (length to diameter) is extremely high.

Nanofilaments in the form of nanotubes have a hollow edge which is on the order of a couple of Angstroms thick. The nanotubes may be either single, double, or multiple walled (i.e., one nanotube within a second, third or further nanotube). For a more comprehensive discussion on carbon nanotubes, see "Carbon Nanotubes Roll On," *Physics World,* June 2000, pages 29–53.

Carbon nanotubes have been proposed as excellent candidates for use as field emitter cathodes due to: (1) the extreme sharpness of their edges and the extremely large aspect ratio, which enable the achievement of low operating voltages; (2) the resistance to tip blunting by residual back ion bombardment due to the uniform wall thickness throughout their height; (3) the relative inertness, high mechanical strength and current carrying capacity; and (4) an inherent current-limiting mechanism in the presence of adsorbed water which retards emitter burn out and destruction by arcing, a problem plaguing the present day FEAs. Nanotubes have been demonstrated in use as a cathode in a cathode lighting element in which the carbon-nanotubes act as the field-emitting cathode.

To be effective emitters, the nanofilaments need to be oriented largely perpendicular to the substrate. Recently, this property has been achieved by growing the nanofilaments on substrates under suitable conditions such as by high temperature chemical vapor deposition (CVD) on catalytic surfaces. For example, CVD has been used to form extremely vertical and uniformly grown carbon nanotubes directly above a metal catalyst substrate of patterned and oxidized iron patches. The resulting nanotubes form an ungated clump electrode which provides a stable field emission over the entire test duration of 20 hours.

On the other hand, high emission current from carbon nanotubes oriented parallel to the substrate has also been observed, which can be attributed to defects on the tube sidewalls. Nanotubes in this orientation can be expected to erode more quickly than those oriented perpendicular to the substrate by residual back ion bombardment.

However, these nanofilament electrodes are not gated and thus, have limited practical use as field emitters. In order to use nanofilaments as a field emitter, one must control the operating characteristics of the nanofilaments, i.e., the turning on and off of small selected groups (i.e. clumps) of nanofilament emitters which comprise an array of emitter cells (e.g. pixels). This control is accomplished by providing a gate electrode, whose applied voltage bias controls the turning on, turning off and the field emission current magnitude. In order to enable low voltage operation, it is necessary to provide a control gate in very close proximity to a group of nanofilament emitters.

One proposed method of forming a gated nanofilament field emitter includes pre-positioning a paste layer of the

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nanotubes separately on a substrate and assembling a control grid gate assembly to the paste layer of nanofilaments. This and other presently available manufacturing techniques (all non-integral) fail to provide practical (e.g., in terms of functional and economical) gating of nanofilaments, e.g., nanotube, field emitters.

One clear disadvantage of this method is that the resulting gated unit tends to be large when compared to integrally formed conventional field emitter cells, which limits the resolution. As a result of the increased emitter-grid gate separation, these grid-gated emitters require a much higher gate voltage (hundreds of volts as compared to tens of volts for integrally gated emitters) for their operation.

An additional disadvantage with presently available carbon nanotube field emitting cathodes is that the grid-type control gates and nanotube cathodes are not self-aligned with one another because the control grid gate is assembled to the nanotubes after a paste layer of nanotubes has already been formed. As a result, the gate current (e.g.: current intercepted by the gate) tens to be very high which can cause overheating. In addition, this approach generally does not provide precise control and operation of the FEA and in particular, precise control of individual cells forming the emitter array, as compared to integrally formed and self-aligned control gate and cathode design.

BRIEF SUMMARY OF THE INVENTION

In accordance with the present invention, a self-aligned, integrally gated nanofilament field emitter cell and array is provided wherein a nanofilament cathode (in the form of a group or "clump" of nanofilaments) and control gate are formed through the microprocessing techniques of the subject invention, thereby self-aligning the nanofilament cathode with the control gate.

According to one aspect of the invention, a field emitter cell is provided which comprises an electrically conductive substrate layer. An insulator layer is disposed directly upon the substrate layer and an electrically conductive gate layer is disposed directly on the insulator layer. An aperture on the gate layer extends through the insulator layer to the substrate layer. A catalyst layer is applied to a surface conductively associated with the substrate layer. Electrically conductive nanofilaments are grown on the catalyst layer. The group of nanofilaments are electrically isolated from the gate. When the field emitter cell is operational, the group of nanofilaments act as a cathode.

In alternate embodiments, the catalyst layer upon which the nanofilaments are grown is applied to top surfaces of various structures which comprise a post structure, a tip structure, and an obelisk structure extending from the substrate surface.

One advantage of the present invention is that a field emitter cell is provided in which the cathode comprising a group of nanofilament emitters in close proximity to a control gate (electrodes). As a result of this close proximity, in conjunction with the extreme nanofilament tip sharpness, the control gate electrodes use a much lower emitter operating voltage as compared with currently demonstrated nanofilament grid-gate or ungated field emitter designs.

Yet, another advantage of the present invention is the resistance of the nanofilaments to blunting by residual back ion bombardment because the edge will remain at the same sharpness due to the uniform thickness throughout their heights. Yet, another advantage of the present invention is that the carbon nanotube has a relatively clean and inert surface (i.e. no non-volatile oxides), which enhances higher

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emission stability. Another advantage is that often these nanofilaments either possess or can be tailored to posses significant resistance which, during emission, will lead to an IR (current times resistance, from the equation V=IR where V=voltage, I=current, and R=resistance) drop in the potential between the gate and the emitter, thereby preventing emitter burn-out by limiting the current. Further, carbon nanotubes, in the presence of adsorbed water, provide an inherent current-limiting mechanism which tends to retard emitter burn-out as disclosed in "Current Saturation Mechanisms In Carbon Nanotube Field Emitters," *Applied Physics Letters,* volume 76, no. 3, Kenneth A. Dean and Babu R. Chalamala, Jan. 17, 2000, herein incorporated by reference.

It is an object of the present invention to provide a self-aligned integrally gated nanofilament field emitter cell and array.

It is an another object of the present invention to provide a integrally gated (but not necessarily self-aligned) nanofilament field emitter cell and array.

It is another object of the present invention to provide a field emitter cell and array in which the gate electrode is placed in very close proximity to a group of nanofilament emitters.

It is yet another objective of the present invention to provide a field emitter cell and array in which the cathode is resistant to blunting and surface contamination.

It is yet another object of the present invention to provide a field emitter cell and array with a very low turn-on voltage and that has a stable field emission.

It is yet another object of the present invention to provide a field emitter cell and array that is very economical to manufacture because no precise lithography is required. In fact, when using the method of the present invention, no lithography is required in making the field emitter cell and array if a stamping technology is used to make the masks for the etching of the starting apertures.

Further features and advantages of the present invention are set forth in, or apparent from, the description of preferred embodiments which follows.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1(a)–1(g) illustratively depicts the processing steps involved in fabricating a field emitter according to a first embodiment of the present invention;

FIGS. 2(a)–2(g) illustratively depicts the processing steps involved in fabricating a field emitter cell according to a second embodiment of the present invention;

FIGS. 3(a)–3(g) illustratively depicts the processing steps involved in fabricating a field emitter cell according to a third embodiment of the present invention in which the emitter cathode comprises a group of nanofilaments formed on a post structure;

FIGS. 4(a)–4(i) illustratively depicts the steps involved in fabricating the field emitter cell according to a fourth embodiment of the present invention in which the emitter cathode comprises a group of nanofilaments formed on a post structure;

FIGS. 5(a)–5(d) illustratively depicts the processing steps in fabricating a field emitter cell according to a fifth embodiment of the present invention in which the emitter cathode is formed as a group of nanofilaments on a conical tip or a tip-on-post emitter structure;

FIG. 5(e) is a plot of the resulting field emission data of the fifth embodiment; and

FIG. 6(a) illustratively depicts a sixth embodiment of a field emitter using a group of nanofilaments as the emitter

cathode with an offset control gate according to the present invention, and FIG. 6(b) is a plot of the field emission data of the sixth embodiment.

DETAILED DESCRIPTION OF THE INVENTION

1st Embodiment

Referring now to FIGS. 1(a)–1(g), illustratively depicted therein are the steps of fabricating a field emitter cell 100 according to the first embodiment of the present invention. The field emitter cell 100 is formed on a conductive or semiconductive substrate layer 102. Optimally, substrate layer 102 is a porous silicon substrate with a nanoporous layer in order to provide for highly directional nanotube growth.

A catalyst layer 104 is deposited on substrate layer 102 by sputtering or evaporative deposition of a suitable catalyst material. The catalyst layer promotes the growth of nanofilaments of interest under appropriate growth conditions (described below). For carbon nanotube growth, the most effective catalyst layer may comprise iron, nickel or cobalt.

Optionally, at this point, the catalyst-coated substrate may be annealed in air to anneal and oxidize the catalyst layer 104. Alternatively, the annealing/oxidation of catalyst layer 104 may be done later or it may be left unoxidized. Insulator layer 106, composed of SiO_2 or other suitable insulator material, is deposited to a few thousand Angstroms thick.

Gate layer 108 is then deposited on insulator layer 106. Gate layer 108 is composed of either a semiconducting material, a metal, or a multiple layer conductive material that does not catalyze nanofilament growth. For example, the material of gate layer 108 may comprise two layers including a chromium layer on a p-type polysilicon layer deposited over the insulator layer 106.

Gate aperture 110 is formed by patterning and etching using any of a number of techniques known in the art such as the one described in the commonly-owned U.S. Pat. No. 6,084,245, herein incorporated by reference. For example, circular posts of resist (not shown) are patterned and fabricated on the gate layer 108 followed by evaporation deposition of a thin chromium layer and then lift-off of the resist post to leave patterned circular apertures in the chromium layer (not shown). Using the chromium layer as an etch mask, standard reactive ion etching (RIE) is used to anisotropically etch aperture 110 through gate layer 108 and insulator layer 106, terminating on the catalyst layer 104.

Referring now to FIG. 1(b), preferably a CVD method is used to deposit a conformal, stand-off layer 112 on the horizontal surfaces 109 of gate layer 108 and along the vertical sides of gate layer 108 and insulator layer 106 and the horizontal surface of catalyst layer 104 exposed during the etching of aperture 110. The thickness of stand-off layer 112 is adjusted to reduce the diameter of aperture 110. Referring now to FIG. 1(c), standard anisotropic RIE of the stand-off layer is carried out to remove the stand-off layer 112 disposed on the horizontal surface 109 of gate layer 108. In addition, RIE removes stand-off layer 112 deposited at the bottom of aperture 110, thereby exposing catalyst layer 104.

If catalyst layer 104 was not previously annealed and oxidized prior to stand-off layer 112 deposition, cell 100 is optionally annealed in air at a temperature to substantially oxidize the exposed catalyst layer 104 as previously described.

Referring now to FIG. 1(d), nanofilaments are grown on top of the exposed catalyst layer 104 disposed at the bottom

of gate aperture 110. Nanofilaments 114 are grown, preferably, perpendicular to and in selective areas over the catalyst surface 104 using growth conditions known in the art, such as those described in connection with the method discussed in *Science*, Vol. 283, 512 (1999) by S. Fan et al., herein incorporated by reference.

Nanofilaments 114, composed of carbon nanotubes, initiate growth on the iron/iron oxide particles that form catalyst layer 104. Optimally, the nanofilaments 114 are grown to the level of gate layer 108 or slightly below, although they may also be at a higher level than the gate layer 108.

Nanofilaments 114, composed of carbon nanotubes, should be grown under conditions that do not form non-nanofilament carbonaceous material on surfaces that do not contain a catalyst. For example, a low hydrocarbon-to-reducing gas ratio should be used in a CVD method.

If needed, cleaning/clearing debris from the top surfaces of field emitter cell 100 such as horizontal surfaces 109 and the horizontal surface 113 of stand-off layer 112, may be accomplished by first filling gate aperture 110 with a protective layer such as a resist or silicon dioxide, followed by perpendicular RIE using oxygen to remove any carbonaceous layer and to etch away the top surface until the residual debris layer is removed.

Referring now to FIG. 1(e), field emitter cell 100 is optionally dipped in a buffered hydrofluoric (HF) solution to remove the upper portion of stand-off layer 112. The hydrofluoric acid removes a portion of the stand-off layer 112 along with cutting into (i.e., removing) a portion of insulator layer 106 adjacent nanofilament clump electrode 116 in areas 118. The hydrofluoric acid is removed by gentle rinsing or weak sonication in distilled water.

Optimally, residual water in the cells is removed through a process of freeze-drying. During the freeze-drying, residual water is removed by sublimation. The freeze-drying minimizes the sticking of the individual nanofilaments 114 to the sidewall(s) of the aperture after a wet treatment. An alternative method of drying is by critical point drying, a technique commonly used to preserve mechanical integrity of biological specimen, in which the water is first replaced with a solvent which is then replaced with a liquefied gas (e.g., carbon dioxide). Minimum distortion occurs upon vaporization of the liquefied gas.

A portion of unanchored or weakly anchored nanofilaments 114 may be dislodged during the hydrofluoric acid and water rinse. Mechanical and electrical anchoring of the remaining attached nanofilaments to the FEA 100, can be enhanced by electroplating with nickel at the base where the nanofilaments 114 meet catalyst layer 104.

Referring now to FIG. 1(f), if nickel plating is desired, a sufficiently long hydrofluoric acid dip/rinse is first conducted to remove stand-off layer 112 from within aperture 110, thereby exposing catalyst layer 104. Subsequently, nickel 120 is plated up from the freshly exposed portions of the catalytic layer 104 at the bottom of aperture 110.

An alternative to the afore-mentioned HF treatment to remove the top portion of the stand-off layer 112 is by dry etching such as reactive ion etching, thereby avoiding the problem of stiction which would cause the nanofilaments to stick to the sidewalls of the aperture after a wet treatment.

Referring now to FIG. 1(g), along with FIGS. 1(e) and 1(f), the resulting field emitter 100 has a gate layer 108 with a circular gate aperture 110. Clump electrode 116 forms the emitter portion consisting of a group of nanofilaments 114 with circular symmetry centered within gate aperture 110.

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Vacuum gap 122 is disposed between the top portion of clump cathode 116, insulator layer 106, and the edge of the gate aperture 110, electrically isolating the nanofilament emitters from the gate. Electrical contact is established between the clump cathode 116, substrate 102, and any layers there between.

Operation of field emitter cell 100 involves the application of a positive voltage bias to the gate layer 108 relative to the clump cathode 116 to extract field emission of electrons from the clump cathode 116. Electrons may be collected on an anode (not shown) placed at a distance above the field emitter array device 100.

Many modifications may be made to this first embodiment to accommodate various manufacturing processes and operating conditions. For example, although nanofilaments 114 are composed of carbon nanotubes, alternate nanofilaments may be nanowires composed of Si, Ge, SiC, GaAs, GaP, InAs, InP, ZnS, ZnSe, CdS, CdSe, MoS_2, WS_2, and combinations thereof grown under appropriate growth conditions known in the art.

In addition, although clump cathode 116 is formed as a circular group of nanofilaments 114, other geometrical shape may be substituted, such as but not limited to, linear, square, and rectangular (not shown) by making appropriately modifications to the method described above. As is obvious to one of ordinary skill in the art, the placement and shape of the starting template structures (e.g. aperture) on the substrate determines the location and shape of resulting emitter cathodes, cells, and array.

2nd Embodiment

FIGS. 2(a)–2(g) there is illustratively depicted a second embodiment which differs from the first embodiment in that in the second embodiment, catalyst layer 204 is deposited after gate layer 208 and stand-off layer 212 is deposited and etched. Therefore, the various processing steps of the second embodiment are the same as in the first embodiment unless otherwise noted.

Insulator layer 206 is deposited directly on substrate layer 202 by any suitable manner known in the art. Subsequently, gate layer 208 is formed on insulator layer 206, and gate aperture 210 is patterned and etched. Stand-off layer 212 is deposited along the surface of cell structure 200 which includes along the gate layer horizontal surface 209, the vertical wall surfaces within gate aperture 210 and along surface 203 of substrate 202 exposed during the etching of gate aperture 210 (FIG. 2(b)). Next, stand-off layer 212 is removed from the horizontal surfaces of cell structure 200, namely gate layer horizontal surface 209 and substrate surface 203, using an anisotropic RIE (FIG. 2(c)).

Catalyst layer 204 is directionally deposited along surface 203, and along the horizontal surface 209 of gate layer 208. In addition, some catalyst material may be residually deposited along the vertical wall surfaces within gate aperture 210 (FIG. 2(d)). Catalyst layer 204 may be composed of the same material as in the first embodiment. Optimally, the material of gate layer 208 passivates the material of catalyst layer—that is, under the nanofilament growth conditions, the catalyst layer on such a gate material no longer catalyze growth of nanofilaments. However, it is not necessary for the material of gate layer 208 to passivate the catalyst in this 2nd embodiment.

Catalyst material deposited on gate layer 208 and the top portion of the vertical side wall of stand-off layer 212 is removed while leaving catalyst layer 204 intact at the bottom of gate aperture 210 on substrate surface 203. Two

methods may be used to accomplish this. The catalyst layer 204 at the bottom of gate aperture 210 is protected by first spinning a resist layer 224 over the field emitter 200 (FIG. 2(d)). Next, isotropic etching with oxygen plasma or anisotropic oxygen RIE removes most of the resist layer 224 except for a portion on top of catalyst layer 204 at the bottom of gate aperture 210. Subsequently, acid dissolution removes catalyst layer 204 from all surfaces not protected by resist 224 (FIG. 2(e)).

Alternatively, rather than depositing resist layer 224 followed by isotropic etching using oxygen plasma, catalyst layer 204 may be selectively removed from all surfaces except from the bottom of aperture 210 by glancing angle sputtering.

Nanofilaments 214 are grown (FIG. 2(f)) and field emitter 200 is then dipped in hydrofluoric acid, rinsed in water, and freeze-dried (FIG. 2(g)). The hydrofluoric acid rinse removes the upper (i.e., top) portion of stand-off layer 212 and undercuts insulator layer 206 in area 218. As with the first embodiment, the base of clump cathode 216 between nanofilaments 214 and the side-wall of aperture 210 may be optionally reinforced as described above. Alternatively, the upper portion of standoff layer 212 can be removed by dry etching, which least disturbs the nanofilaments.

3rd Embodiment

Referring now to FIGS. 3(a)–3(g), in a third embodiment, the starting substrate upon which the nanofilaments are grown is a post structure 330. Referring now specifically to FIG. 3(a), post 330 is formed by patterning and reactive ion etching (RIE) a starting material of nanoporous silicon layer substrate 302 with catalyst layer 304. The patterning and RIE are standard microelectronic fabrication methods known in the art. Catalyst layer 304 is optionally oxidized in the same manner as in the earlier described embodiments.

Nanofilaments 314 are preferably carbon nanotubes that are grown on top of post 330 under the same conditions as in the previous embodiments, resulting in clump cathode 316 (FIG. 3(b)). A conformal stand-off layer 312 composed of silicon nitride, silicon dioxide or tungsten, is deposited over the entire cell structure 300 structure (FIG. 3(c)).

Referring now to FIG. 3(d), planarization layer 332 is deposited over cell structure 300 along the top of stand-off layer 312. Planarization layer 332 is composed of a suitable insulator material such as silicon dioxide or spin-on glass of a different insulator material than that of stand-off layer 312. Standard planarization techniques such as chemical-mechanical-polishing (CMP) is performed on planarization layer 332 (FIG. 3(d)).

Selective directional RIE is used to etch back planarization layer 332 to a desired height 334 below the top of stand-off layer 312 without etching the stand-off layer 312 (FIG. 3(e)). The desired height 334 determines the placement of the control gate relative to clump cathode 316.

Referring now to FIG. 3(f), gate metalization material is directionally evaporated on top of planarization layer 332 to form gate layer 308, and on the horizontal surface of stand-off layer 312 to form metalization cap 338. Care should be taken such that gate metalization material is not deposited on the vertical portions 313 of stand-off layer 312. If necessary, a short etch may be used to remove any material inadvertently deposited on the vertical portions 313 of stand-off layer 312.

Wet etch (such as by HF) or isotropic dry etch is carried out to remove the top portion 336 of stand-off layer 312. The wet etch or isotropic dry etch also removes metalization cap

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338 as well as removing a portion of stand-off layer 312 below metalization cap 338, recessing stand-off layer 312 sufficiently below the top of clump cathode 316 (FIG. 3(g)). If a wet etch is used, freeze-drying is used to remove the residual liquid.

4th Embodiment

Referring now generally to FIGS. 4(a)–4(i), a fourth embodiment is shown which represents a modification of the processing method of the third embodiment. In the fourth embodiment, a catalyst layer 404 is deposited on post 430 after gate layer 408 is formed.

Referring specifically now to FIG. 4(a), post 430 is formed in a similar manner as post 330 with the exception that the starting structure is a post structure 430 on top of substrate 402 without a catalyst layer formed thereon. A silicon dioxide (SiO₂) stand-off layer 412 is thermally grown (in case if the post and substrate are made of silicon) or deposited over cell structure 400 including the horizontal surfaces 403 of substrate 402 and horizontal and vertical surfaces of post 430 (FIG. 4(b)). Subsequently, planarization layer 432, composed of SiO₂, gate layer 408 and metalization cap 438 are formed as in the third embodiment (FIG. 4 (c)). A wet etch in buffered HF or isotropic dry etch removes the metalization cap 438, the top portion of the stand-off layer and undercuts planarization layer 432 in areas 418 (FIG. 4(d)).

A thin, conform CVD silicon dioxide forms sacrificial layer 440 (FIG. 4(e)) over all surfaces of the cell. Next, directional RIE is used to remove sacrificial layer 440 from the top of post 430 and the top of gate layer 408 while leaving the vertical sides of post 430 covered with the CVD silicon oxide sacrificial layer 440 (FIG. 4(f)).

Referring now to FIG. 4(g), catalyst layer 404, such as nickel (Ni) which is relatively resistant to reaction with HF is directionally deposited by sputtering or evaporation on the top surfaces of cell structure 400 which include on top of post 430 and gate layer 408, as well as residually in gate aperture 410 along conformal sacrificial oxide layer 440. Optimally, under nanotube growth conditions, the material of gate layer 408 should alloy with the material of catalyst layer 404, or in the alternative, material of gate layer 408 should passivate the material of catalyst layer 404, thereby preventing nanofilament growth on gate layer 408. For example, the gate material may be chromium (Cr) which passivates Ni.

The field emitter 400 is briefly dipped in a dilute buffered HF solution to remove (i.e., lift off) any catalyst material which may lie on top of the sacrificial silicon dioxide layer 440 in gate aperture 410 (FIG. 4(h)). The hydrofluoric acid removes both the unwanted catalyst present in aperture 410 as well as CVD silicon dioxide sacrificial layer 440 present in aperture 410 along the vertical wall surfaces of post 430 and along planarization layer 432 and gate layer 408. A significant amount of catalyst should remain on the top surface of the post 430.

Nanofilaments 414, preferably carbon nanotubes, are grown on top of post 430 under similar conditions as set forth in the previous embodiments, resulting in clump cathode 416 (see FIG. 4(i)).

One advantage of the fourth embodiment is that the nanofilament 414 placement can be above gate layer 408. Consequently, there is less of a chance that there will be a short between nanofilaments 114 and gate layer 408.

5th Embodiment

FIGS. 5(a)–5(d), depicted a fifth embodiment of the present invention. In this embodiment, nanofilament growth

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occurs on the top surface of a conventional tip-on post emitter (530) or conical tip emitter (531) known in the art. This embodiment differs from the fourth embodiment in that instead of using the blunt post structure of post 430, this embodiment uses ready-made conventional field emitter structures of sharpened tip-on-post structure or a conical tip structure upon which nanofilaments are grown. Otherwise, the processing steps of this embodiment are identical to that of the fourth embodiment.

The formation of nanofilaments along the top of tip-on post 530 and conical tip 531 occurs in the same manner as in the fourth embodiment. Specifically, a conformal silicon oxide sacrificial layer is first deposited over field emitter cells 500, 501,and then selectively removed by directional RIE from the top surfaces of the tip-on-post 530, or conical tip 531, in a manner similar to that in the fourth embodiment. Optimally, the gate aperture 511 of the conical tip design is small as practicable and should be smaller than the diameter of the base of the conical cathode 531.

Next, a catalyst is deposited, the sample treated with hydrofluoric acid, rinsed in water, and nanofilaments are grown along the top surface of tip-on-post 530, and conical tip 531 (FIGS. 5(c) and 5(d)), in similar manner as in the fourth embodiment. As a result, clump cathode 516 is formed of nanofilaments 514 protruding outward from the surface of the centers (i.e., upper portions) of tip-on post 530 (FIG. 5(c)) and conical tip 531 (FIG. 5(d)).

The lengths of the nanofilament 514 should be limited so that the nanofilaments are relatively short and do not come into contact with other parts of the emitter (for example, the gate layer 508 or insulator 532). Preferably, the lengths of the nanofilaments should be a small fraction of the distance between the top of the original (tip-on- post or conical tip) to the edge of the gate aperture 510 and 511. Optimally, although not essential, tip-on post 530 and conical tip 531 should be of a material that does not passivate the catalyst material 504.

If the emitter tip material passivates the catalyst, the tip should be coated with a material that prevents diffusion of the catalyst material into the tip material under nanofilament growth conditions. As with the previous embodiments, it is preferable that the material of gate layer 508 does passivate the catalyst material so that no nanofilaments will grow on the gate layer 508.

If the gate material does not passivate the catalyst material, it is necessary to remove the catalyst material from the top surface and the edge of the gate. Sputtering at a glancing angle (small angle relative to the surface of the substrate) with an ion beam is one such way of removing the catalyst material. Care should be taken that the angle is such that no portion of the tip-on-post or conical tip is sputtered.

To remove catalyst material from any silicon dioxide surface (for example, on the top surface or oxide insulator surface 532 or along the shank portion of conical portion tip-on post 530), the structure may be dipped in a buffered HF solution. However, the duration should be sufficiently short such that a significant amount of catalyst 504 still remains on the surfaces of the top portions of structures 530 and 531.

Optimally, nanofilaments 514 are grown on the portion of tip on-post 530 and conical tip 531 covered with catalyst layer 504 using CVD method under lean hydrocarbon conditions (i.e., low hydrocarbon-to-reducing gas ratio) to eliminate growth of non-nanofilament carbonaceous material on insulator layer 532. The growth time should be limited so that nanofilaments 514 should be relatively short.

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If necessary, a short isotropic oxygen plasma, such as in a barrel etcher, can be used to remove any thin layer of carbonatious material from insulator layer 532. If the insulator layer 532 is silicon dioxide, it can be optionally followed by a short dip in dilute buffered HF and subsequent water rinsed to ensure cleanliness of the surface of insulator 532.

Precautions should be taken to prevent any nanofilaments 504 from lying down on the tip surface due to adhesion (stiction) after exposure to an aqueous environment of HF and water rinse. As with the previous embodiments, it is optimal to use a freeze-drying or a critical-point drying technique.

An exemplary preferred implementation of the processing method of the fifth embodiment will now be considered. It will be understood that this example is provided to enhance understanding of the present invention and not to limit the scope or adaptability thereof.

The starting structures were an array of the silicon tip-on-post gated field emitter cells fabricated according to a process developed at the Microelectronic Center of North Carolina by a number of standard silicon microprocessing steps (outlined in FIG. 3 in D. Temple, et. al., J. Vac. Sci. Technol. B 13, 150 (1995) and in FIG. 2 in L. N. Yadon, et. al., J. Vac. Sci. Technol. B 13, 580 (1995)). The silicon tip-on-post emitter cell structure is schematically shown in FIG. 5(a) of the present disclosure.

The silicon post height was about 4 microns, the post diameter was about 1 micron, and the post was topped with a very small and sharp conical silicon tip. The gate aperture diameter was 2.8 microns and the gate material was made of pure chromium, which apparently could survive the relatively high temperatures and conditions used for carbon nanotube (cNT) growth in the current example. Moreover, chromium, under the cNT growth conditions used in this example, has been observed to passivate Fe and Ni catalysts (e.g. no cNT growth on Fe and Ni-coated chromium surfaces). Since the sidewalls of the tip-on-post structure had some silicon dioxide left on it from processing, it was optional to omit the initial deposition of a conformal sacrificial silicon dioxide layer. In this example, the initial conformal silicon dioxide sacrificial layer had been omitted.

Next, a very thin layer of nickel catalyst was sputter-deposited on the substrate using an ion beam and a nickel foil as sputtering target. The nickel coated the surfaces of the chromium gate, the top surface of the tip-on-post (including the small silicon tip), and likely residually other surfaces in the emitter cell cavity. The sample was then briefly dipped in a dilute buffered HF solution and thoroughly rinsed (by weak ultrasonication) in distilled water. The HF removed much (by lift-off) much of the residual nickel that happened to be on any silicon dioxide surfaces in the emitter cell cavity. After drying by blowing with nitrogen and mild heating on a hot plate, the sample was placed on the flat top of a molybdenum cartridge heater in a hot filament chemical vapor deposition (CVD) flow reactor, in which the hot filament consisted of a tungsten ribbon suspended parallel to and about a centimeter above the sample. The cartridge heater and the tungsten filament were heated separately. The temperature was measured by a thermocouple in contact with the top surface of the cartridge heater. The gas flow was perpendicular to the surface of the sample.

Growth of the carbon nanotube emitters began by first heating the sample in flowing argon at a pressure of about 20 torr until a temperature of about 700° C. was reached, at which ammonia gas at a flow rate of 80 sccm replaced the

argon and flowed onto the sample. The hot filament was immediately turned on and maintained at a filament temperature of about 1900° C. as monitored by an optical pyrometer. Five minutes after turning on the hot filament, ethylene gas at a flow speed of 20 sccm was admitted into the flow reactor. The final temperature and pressure were maintained at 683° C. and 23.3 torr, respectively. The hot filament, the ethylene gas, and ammonia gas were shut off 4.5 minutes after the admission of the ethylene gas. Argon at about 25 torr was then flowed as the sample was cooled down slowly.

Scanning electron microscope examination showed carbon nanotubes on the top surface of the tip-on post cathode structure and no carbon nanotubes on the chromium gate.

The sample was subjected to field emission test in an ultra-high vacuum chamber equipped with electrically conductive cathode, gate, and anode probes to provide electrical contact to the individual pixels (arrays) of the field emitter and to measure the current of the field-emitted electrons. For a pixel consisting of 33,000 emitter cells, the collected emission current (anode current) was measured as a function of the voltage applied to the gate electrode (with the cathode at ground). The results are shown in FIG. 5(e).

An important result is the low turn on voltage (e.g. ~17 volts) compared to about 80 volts obtained for an array of silicon tip-on post FEA (without the nanotubes). The result for the latter sample is consistent with the 80–90 volts required by the silicon tip-on post structures in references by D. Temple, et. al., and L. N. Yadon, et. al. (above mentioned). This low turn-on voltage for the present nanotube-decorated example can be attributed to the carbon nanotubes acting as field emitters.

There can be a wide latitude on the growth parameters, such as different catalysts (e.g. Fe, Co), temperatures (500–1000° C.), hydrocarbons (e.g. methane, acetylene), reducing agents (hydrogen), flow rates, pressures, and even a variety of growth techniques including thermal, microwave, and RF CVD methods as well as arc and laser-assisted catalytic growth methods. In a CVD method, a low hydrocarbon-to-reducing agent ratio is necessary to minimize amorphous carbon deposition on catalyst-free surfaces, to avoid electrically shorting out the emitter cell (between cathode and gate).

6th Embodiment

In a sixth embodiment, the control gate is formed as offset gate aperture 609 in which the gate aperture is offset by distance 650 from the edge of the aperture 611 in insulator layer 606 (see FIG. 6(a). The offset of a gate aperture from that of the insulator layer has previously been described in patent application Ser. No. 09/478,899 filed on Jan. 7, 2000, herein incorporated by reference.

The sixth embodiment is based on the second embodiment. All processing steps are the same as those in the second embodiment except that the starting cell structure has an off-set gate aperture. A similar offset of gate aperture 609 from the insulator aperture 611 formed therebelow may also be incorporated into the other embodiments. Likewise, other embodiments of gate offset in patent application Ser. No. 09/478,899 are also incorporated into the present embodiment and other embodiments of the present invention as applicable. One possible advantage of having an offset gate layer is to reduce the gate current by precluding a direct-line-of sight from the nanofilament emitter to the gate.

An exemplary preferred implementation of the processing method of the sixth embodiment will now be considered. It

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should be understood that this example is provided to enhance understanding of the present invention and not to limit the scope or adaptability thereof.

The starting structure was similar to that shown in FIG. 2(a), except that the gate was offset (having a larger diameter than that of the hole in the insulator layer). The methods for fabricating starting structures with offset gates were also given in a commonly-owned patent application (patent application Ser. No. 09/478,899). The gate material consisted of a 60 nm thick chromium layer on top of a 150 nm thick p-type silicon layer. The hole in the insulator layer had a diameter of 1.2 microns and the gate diameter was 2.25 microns (e.g. the offset was about 0.5 micron). A stand-off CVD silicon dioxide layer (nominally 0.42 micron thick on top flat surface) was then deposited over the structure, followed by oxide etch back by RIE of 0.45 micron of silicon dioxide. SEM analysis showed a 0.32 micron thick stand-off layer on the vertical sidewall of the hole, leaving an open, inner hole of about 570 nm diameter.

A thin layer of Fe was then deposited over the sample using an ion beam and a Fe foil as sputtering target. Next, a 0.25 micron thick Shipley 1400 photoresist was spin-coated over the sample, followed by baking at 90° C. for 30 minutes. Oxygen plasma using a barrel etcher was used to remove the resist from the top horizontal surface and from the upper portion of the hole. The exposed Fe was removed by dipping the sample in an acid solution. After rinsing in water and drying, the sample was ultrasonicated in acetone, followed by ethanol to remove the resist from the bottom portion of the hole, thereby exposing the Fe catalyst on the bottom portion of the hole.

The growth of the carbon nanotube emitters was carried out under similar conditions as described above in reference to the exemplary implementation of the fifth embodiment, except that a DC voltage bias was placed on the hot filament with respect to the top surface of the cartridge heater and that a growth duration of only 40 seconds was used. The purpose of the voltage bias was to promote more oriented growth of the carbon nanotubes.

Field emission test was carried out on a small pixel of an array of 20 emitter cells. The anode current and the gate current were measured simultaneously as a function of the voltage applied to the gate electrode. The results are shown in FIG. 6(b). A turn-on voltage below 35 volt was observed. FIG. 6(b) also shows that the gate current is a very small fraction of the anode current, a result expected from an offset gate design. An offset gate can also be expected to require a higher turn-on voltage than one without an offset.

Alternative photoresist etching could be done by oxygen reactive ion etching (which is anisotropic) instead of by the oxygen barrel etcher (which is isotropic), thereby gaining better control over the portion of resist to be removed.

Although the invention has been described above in relation to preferred embodiments thereof, it should be understood by those skilled in the art that variations and modifications can be effected in these preferred embodiments without departing from the scope and spirit of the invention.

What is claimed is:

1. A field emitter cell comprising:

an electrically conductive substrate layer;

an insulator layer formed on a surface conductively associated with said substrate layer, said insulator layer having a first aperture therethrough, said aperture defined by a sidewall and a bottom surface, said bottom surface conductively associated with said substrate layer;

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an electrically conductive gate layer disposed on said insulator layer thereby forming an electrically conductive gate, said electrically conductive gate having a second aperture;

a catalyst layer conductively associated with said substrate layer; and

an electrically conductive group of nanofilaments grown upon said catalyst layer and conductively associated with said substrate layer, said group of nanofilaments being electrically isolated from said gate, said gate and said group of nanofilaments being self-aligned with one another.

2. The field emitter cell of claim 1, wherein said catalyst layer is formed directly on said substrate layer.

3. The field emitter cell of claim 1, wherein said surface upon which said insulator layer is formed comprises an upper surface of said substrate layer.

4. The field emitter cell of claim 1, wherein said surface upon which said insulator layer is formed comprises an upper surface of said catalyst layer.

5. The field emitter cell of claim 1, wherein said nanofilaments comprises carbon nanotubes.

6. The field emitter cell of claim 1, wherein said nanofilaments comprises nanowires composed of material selected from the group consisting of doped or undoped Si, Ge, SiC, GaAs, GaP, InAs, InP, ZnS, ZnSe, CdS, CdSe, MoS_2, WS_2, and combinations thereof.

7. The field emitter cell of claim 1, wherein said gate layer is a passivating gate material upon which a predeposited catalyst material does not catalyze growth of nanofilaments under nanofilament growth conditions.

8. The field emitter cell of claim 1, wherein said gate layer is a passivating gate material selected from the group consisting of Cr, W, Pt, Ta, Mo, and combinations thereof.

9. The field emitter cell of claim 1, further comprising a vacuum gap separating said nanofilaments from said gate.

10. The field emitter cell of claim 1, further comprising a stand-off layer disposed between said group of nanofilaments and said sidewall of said insulator layer.

11. The field emitter cell of claim 10, wherein said stand-off layer is insulating and is either recessed or not recessed.

12. The field emitter cell of claim 10, wherein said stand-off layer is conducting and is recessed.

13. The field emitter cell of claim 1, wherein said group of nanofilaments form a cathode.

14. The field emitter cell of claim 1, wherein said gate is integrally formed, wherein at least one aspect of the geometry or placement of either the group of nanofilaments or the gate is manipulated to determine the geometry or placement of the other, relative to each other.

15. The field emitter cell of claim 1, further comprising a post-structure extending from a substrate surface, and upon which said catalyst layer is formed, and wherein said gate, said post-structure, and said group of nanofilaments are self-aligned with one another.

16. The field emitter cell of claim 15, wherein said post-structure is tapered on an end forming a conical tip opposite said substrate layer and said catalyst layer is formed on said end of said post-structure opposite said substrate layer.

17. The field emitter cell of claim 16, wherein said gate, said post structure, and said group of nanofilaments are self-aligned with one another.

18. The field emitter cell of claim 1, further comprising a conical tip structure extending from a substrate surface and upon which said catalyst layer is formed.

19. The field emitter cell of claim 18, wherein said gate, said tip structure, and said group of nanofilaments are self-aligned with one another.

20. The field emitter cell of claim 1, wherein said second aperture is coincident with said first aperture.

21. The field emitter cell of claim 1, wherein said gate aperture is offset from said first aperture, said gate aperture being greater than said first aperture.

22. The field emitter cell of claim 1, wherein size of said gate aperture is smaller, equivalent, or larger than said first aperture in said insulator layer, and said gate aperture having a standoff insulator layer shielding the gate layer to preclude a direct line-of-sight from nanofilament emitter.

23. The field emitter cell of claim 1, wherein said first aperture and said gate aperture have a geometric shape selected from the group consisting of circular, linear, square, rectangular, and polygonal.

24. The field emitter cell of claim 1, wherein said nanofilament emitter has a sufficient resistance that, during emission, limits the current of the emitter by causing an IR drop in the potential between the gate and the emitter.

25. The field emitter cell of claim 1, wherein said gate layer is a multiple layer structure comprising at least one conducting layer.

26. The field emitter cell of claim 1, wherein said gate layer comprises a p-type semiconductor.

27. The field emitter cell of claim 1, wherein said catalyst layer is formed upon a porous silicon layer, said catalyst layer and said porous silicon layer being conductively associated with each other and with said substrate layer.

28. A field emitter cell comprising:

an electrically conductive substrate layer;

an insulator layer formed on a surface conductively associated with said substrate layer, said insulator layer having a first aperture therethrough, said aperture defined by a sidewall and a bottom surface, said bottom surface conductively associated with said substrate layer;

an electrically conductive gate layer disposed on said insulator layer thereby forming an electrically conductive gate, said electrically conductive gate having a second aperture;

a catalyst layer conductively associated with said substrate layer; and

an electrically conductive group of nanofilaments grown upon said catalyst layer and conductively associated with said substrate layer, said group of nanofilaments being electrically isolated from said gate.

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